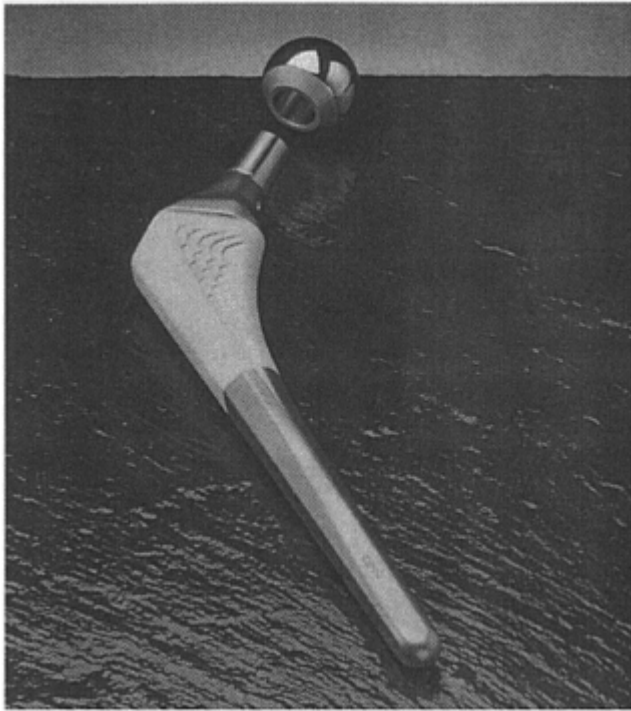


**Advanced Ceramics**  
**Volume 1**  
**BIOCERAMICS**

**James F. Shackelford**

**Gordon and Breach Science Publishers**

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The upper third of the femoral stem in this hip prosthesis is coated with hydroxyapatite for the purpose of improved adhesion between the prosthesis and bone, in which hydroxyapatite is the predominant mineral phase. (Courtesy of Osteonics.)

# **Bioceramics**

# **Advanced Ceramics**

A series edited by Dale Niesz  
Ceramics Department

Rutgers University, Piscataway, New Jersey, USA

This series consists of an extensive compilation of sharply focused tracts covering the many aspects of high-tech ceramics. The goal of this series is to act as a current reference source in providing better understanding of use of these materials in a convenient and practical manner for electrical and mechanical engineers, as well as other technical professionals involved in design and manufacture of state-of-the-art advanced ceramic products.

Volume 1

## **Bioceramics**

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# **Bioceramics**

**James F.Shackelford**

*Division of Materials Science and Engineering  
University of California, Davis, USA*

**Gordon and Breach Science Publishers**

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Printed in Singapore.

Amsteldijk 166  
1st Floor  
1079 LH Amsterdam  
The Netherlands

British Library Cataloguing in Publication Data

Shackelford, James F.  
Bioceramics.—(Advanced ceramics; v. 1)  
1. Ceramics in medicine  
I. Title  
617.9 5

ISBN 0-203-30413-6 Master e-book ISBN

ISBN 0-203-34404-9 (Adobe eReader Format)

ISBN 90-5699-612-6 (Print Edition)

*To*  
*Penelope and Scott*

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# PREFACE

Bioceramics are those engineered materials that are inorganic and nonmetallic in nature and find their applications in the field of medicine. As such, we are placing ceramics in the context of modern engineered materials—distinct from metals, and their alloys, and organic polymers. In this definition, we are considering “ceramics” in a broad sense, including noncrystalline glasses and some ceramic-based composites. The field of biomedical engineering is an inherently interesting one. The subject holds a natural fascination for both engineering students and practicing professionals. I share their enthusiasm for the opportunity to apply our training in engineering to improve the well-being of our fellow men. This is especially true in the area of materials engineering, as many biomedical engineering applications, as is true for general engineering applications, are materials-limited.

The history of bioceramics is especially fascinating. The inherent limitations of the mechanical properties of traditional structural ceramics were associated with the limited use of bioceramics, despite the fact that ceramics are more similar to natural skeletal materials than the more widely used metallic implants. Improvements in ceramic processing technology in the 1960s led to a burst of interest in bioceramics. Despite promising research in the late 1960s and early 1970s, applications in the field progressed slowly. A less conservative governmental regulatory system in Europe led to substantially more clinical experience with bioceramics there. The past decade has seen a renaissance of interest in these materials. This is best illustrated by the increasing use of plasma-sprayed hydroxyapatite coatings on metallic implants. The use of this ceramic, which is the primary mineral content of bone, represents the successful use of an engineered material in conjunction with its natural role in the body. Finally, ceramic processing research has come full circle with the current interest in “biomimetic” materials. In this case, researchers hope to discover ways to produce engineered ceramics with superior mechanical properties at reduced temperatures by imitating the natural processes by which certain ceramic materials are formed in shells and skeletal structures. In turn, these engineered materials would be candidates for medical applications.

Consistent with this series of tracts being produced in conjunction with the American Ceramic Society, this book, *Bioceramics*, is oriented toward the

general reader. I hope my fellow ceramic engineers as well as a much broader audience of professional users of ceramic materials, including mechanical engineers and orthopaedic surgeons, will find this volume useful. Writing this book has been a genuine pleasure consistent with the fascinating nature of the subject. I am especially grateful to those who have been generous in helping to produce this work. I am equally grateful to those with whom I have interacted in this field over the years.

The initial collaborator in this regard was Harry Skinner, MD, PhD, a former classmate who used his training in ceramic engineering as a springboard to orthopaedic surgery. Harry currently serves as chair of the Orthopaedic Surgery Department at the University of California, Irvine. During his residency at the University of California, Davis many years ago, he introduced me to the field of bioceramics and, more broadly, biomedical engineering. Through him, I developed a collaboration with the Orthopaedic Surgery Department here that continues to this day. It has been my great fortune to be associated with the Orthopaedic Research Laboratory that has helped to make the department a premier one in this field. Michael Chapman, MD, chair of the department, and Bruce Martin, PhD, director of the research laboratory, have been especially helpful. In addition, I am indebted to all the faculty, staff and students who have made this interaction both productive and pleasurable.

Finally, I would like to express my gratitude to my publisher and the American Ceramic Society for their patience and support in producing this volume.

# ACKNOWLEDGMENTS

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# CHAPTER 1

## *History and Scope of Biomaterials*

At the outset, we should note that the classification of *biomaterials* appropriately follows the traditional categories of structural materials, viz. *metals*, *ceramics* (and *glasses*), *polymers*, and *composites* (Shackelford 1996). In effect, any structural application for medical purposes makes the engineered material a “biomedical” one. As with the broad treatment of the field of “*materials science and engineering*,” (Shackelford 1996) there is a tendency to focus on metallic materials and then nonmetallic materials in relation to more established metallic applications. A central issue surrounding contemporary engineered materials is “materials substitution.” The use of lower-density polymers and composites in place of metallic auto body panels and the use of more refractory ceramics in place of metallic engine parts are important examples. In this book, dedicated to the topic of “*bioceramics*,” we shall remain aware of the relationship of ceramics to the alternate applications of metals, polymers, and composites in biomedicine.

The history of biomaterials, in general, is often given in terms of metallic implants (Fraker and Ruff 1977). For example, the use of metals for orthopaedic applications dates from ancient times. Up to 1875, relatively pure metals such as gold, silver, and copper were primarily used, but not always with great success due to poor surgical conditions. Engineered metal alloys became more widely used between 1875 and 1925 coincident with substantial improvements in surgical techniques. The period since 1925 can be considered the modern era of metallic biomaterials, with the development of a wide variety of orthopaedic applications for which the dominant alloys of choice are 316L stainless steel, Co-Cr alloys, and Ti-6Al-4V. A typical metal alloy for a modern biomedical application (hip replacement) is shown in [Figure 1.1](#).

Polymeric biomaterials are used in a wide variety of surgical applications, such as blood vessel prostheses, tissue adhesives, heart valves, lenses, and sutures (Ratner 1993). Evidence exists in papyrus records for the use of linen sutures for closing wounds 4,000 years ago. Catgut was introduced for sutures in the second century. Silk was used for this purpose in the 11th century. A variety of contemporary synthetic polymers are now used in modern surgery. Polyethylene, polyester, polyglycolic acid, and nylon are examples. In [Chapter 6](#), we shall focus on the widely used orthopaedic surgery of total hip replacement.



FIGURE 1.1 The stem and ball of this prosthesis for an artificial hip joint are made from a cobalt-chrome metal alloy. The polymer cup which completes the ball and socket system is made of polyethylene. (Courtesy of DePuy Inc.)

Polymethylmethacrylate (PMMA) cement and a polyethylene acetabular cup are routinely used in this application. [Figure 1.1](#) shows a polyethylene cup in conjunction with the metallic stem and ball.

The use of *advanced composites* for biomedical applications has been the focus of much speculation but relatively limited use to date (Devanathan 1991). Carbon fiber-reinforced polymers, for example, have been used for structural applications such as the femoral stem in the total hip replacement. The beneficial feature of being able to control the stem modulus is offset by concerns about physiological reactions to fibers which may be released into the biological environment. Furthermore, the use of these and other “new” materials is more challenging in the United States by the relatively conservative policies of the Food and Drug Administration (FDA). The issue of governmental regulation can also be a factor in the expansion of applications for bioceramics.

In [Chapter 2](#), we shall turn our attention to the historical development of applications in biomedicine for ceramics and glasses. Again, it will be important to maintain a perspective on the applications for the other structural materials reviewed above. The inherent brittleness of traditional ceramics has generally limited their competition with ductile metals and polymers. This is offset by the obvious fact that bone is 43% by weight hydroxyapatite, a common ceramic mineral. Current advances in ceramic processing, including the production of significant improvements in fracture toughness, are contributing to increased possibilities for the inherently attractive use of ceramics in biomedicine.

## CHAPTER 2

### *History and Scope of Bioceramics*

A strong interest in the use of ceramics for biomedical engineering applications developed in the late 1960's, exemplified by the work of Hulbert and co-workers (Hulbert et al. 1982–83). Although that interest reached a plateau during the late 1970's and early 1980's, there is now an increased pace of activity in the field of *bioceramics*. Good examples have been provided recently by various symposia on bioceramics held in a variety of international venues (Bonfield, Hastings, and Tanner 1991; Ravaglioli and Krajewski 1992; Fishman, Clare, and Hench 1995). The development of ceramic material applications in biomedicine has concentrated mostly in orthopaedics and dentistry. Orthopaedic bioceramics provide the advantage of chemical similarity to natural skeletal materials. As with orthopaedic materials, dental applications for ceramics are attractive due to the chemical similarity between engineered ceramics and natural dental materials. In addition, a predominance of compressive loads are present for which ceramics provide their optimal mechanical performance. On the other hand, the mechanical loading for orthopaedic applications tends to include substantial tensile stress components.

Three broad categories of bioceramics have been defined by Hulbert, et al. (1982–83) and are summarized in [Table 2.1](#) and illustrated by [Figure 2.1](#).

Obviously, the categories are based on chemical reactivity with the physiological environment. Relatively *inert* bioceramics, such as structural  $\text{Al}_2\text{O}_3$ , tend to exhibit inherently low levels

TABLE 2.1 Categories of ceramic biomaterials<sup>1</sup>

Category	Example
Inert	$\text{Al}_2\text{O}_3$
Surface Reactive	Bioglass
Resorbable	$\text{Ca}_3(\text{PO}_4)_2$

<sup>1</sup> After Hulbert, et al. 1982–83

of reactivity which peak on the order of  $10^4$  days (over 250 years). *Surface reactive* bioceramics, such as Hench's Bioglass, (Hench et al. 1971) have a substantially higher level of reactivity peaking on the order of 100 days.



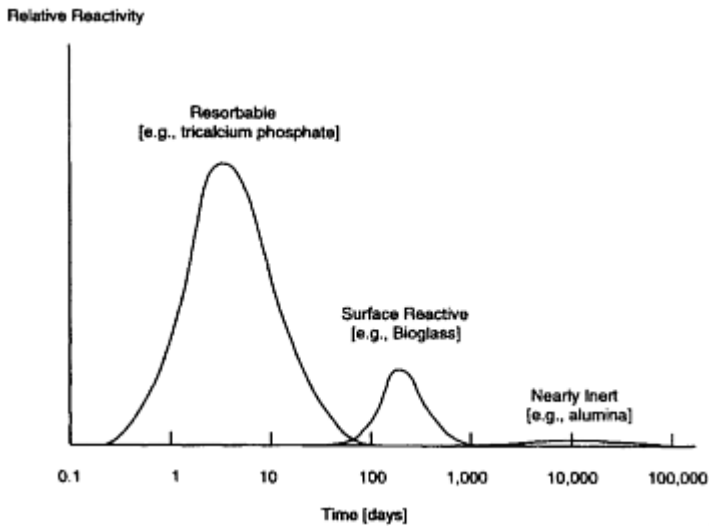


FIGURE 2.1 Bioceramics can be classified into three subgroups, based on their chemical reactivity in a physiological environment. (After Hulbert, et al. 1982–83)

*Resorbable* bioceramics, such as tricalcium phosphate, have even higher levels of reactivity peaking on the order of 10 days. This broad spectrum of chemical behavior has led to a corresponding range of engineering design philosophies.

The history of bioceramics was reviewed in some detail by Hulbert, et al. in the early 1980's (Hulbert et al. 1982–83). For this book, a brief overview is provided primarily to identify the foundations for the range of categories identified in [Table 2.1](#). The first widely evaluated bioceramic was common plaster of Paris,  $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ . Dreesman published the first report on the use of plaster of Paris to repair bone defects in 1892 (Hulbert et al. 1982–83). Extensive studies of plaster of Paris for such applications continued through the 1950's. (Peltier et al. 1957). Attractive features of this material included little or no adverse tissue reaction and its replacement by new tissue at a rate comparable to its absorption by the physiological system. These advantages were offset by an inherent weakness and a rapid degradation in strength during absorption. This trade off between good physiochemical behavior and poor mechanical performance has been characteristic of many biomedical applications of ceramic materials.

The successful use of *tricalcium phosphate*,  $\text{Ca}_3(\text{PO}_4)_2$ , was reported as early as 1920 (Albee and Morrison 1920). In that study, the average length of time for bone defect repair in rabbits was accelerated from 41 days to 31 days. It might be noted that not all calcium salt implantations are successful. For example, numerous studies on calcium hydroxide have indicated that it tends to stimulate the formation of immature bone (Hulbert et al. 1982–83).

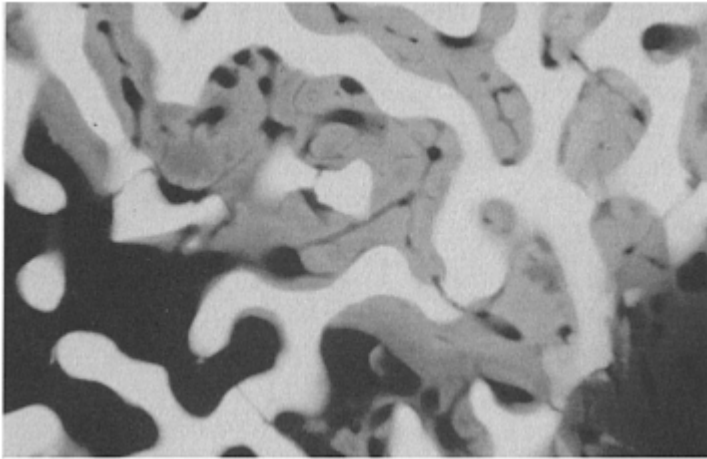


FIGURE 2.2 As seen in this microstructural cross section of a porous hydroxyapatite ceramic, bone can be anchored to a bioceramic by ingrowth when the open porosity exceeds approximately 100  $\mu\text{m}$  in size. Note also [Figure 4.1](#). (Courtesy of R.Bruce Martin)

The “modern” era of bioceramics can be traced to Smith’s successful 1963 study of a ceramic bone substitute named Cerosium, composed of a porous aluminate ceramic impregnated with an epoxy resin (Smith 1963). The porosity of the ceramic was controlled at 48% in analogy to a comparable value for natural bone and in order to produce net physical properties very close to those of bone. Similar modulus and flexural strengths combined with good biocompatibility led to successful bone replacement applications during the remainder of the 1960’s and into the 1970’s. As noted at the opening of this chapter, the widespread interest in biomedicine within the ceramics community developed in the late 1960’s, largely as a result of the extensive work of Hulbert and co-workers (Hulbert et al. 1970; Hulbert 1969; Talbert 1969; Klawitter 1970). The biocompatibility of *oxide ceramics* was convincingly demonstrated, along with the development of the use of bone tissue ingrowth into porous ceramics as a means for mechanically interlocking prostheses. An example of a porous, inert ceramic microstructure is shown in [Figure 2.2](#).

As noted in [Table 2.1](#), one can identify three broad approaches to using engineered ceramics for biomedical applications. Tricalcium phosphate is representative of a resorbable bioceramic. (See [Figure 2.3](#)) The oxide ceramics studied extensively beginning in the late 1960’s represent an opposite strategy, viz. a nearly inert bioceramic. In the early 1970’s, an intermediate approach was developed with the extensive evaluation of surface reactive bioceramics by Hench and co-workers (Hench et al. 1971 ; Hench and Paschall 1973; Piotrowski et al. 1975; Griss et al. 1976; Stanley et al. 1976). The primary development was *Bioglass* ([Figure 2.4](#)), defined as a glass designed to bond directly to bone by providing surface reactive silica, calcium, and phosphate groups in an alkaline

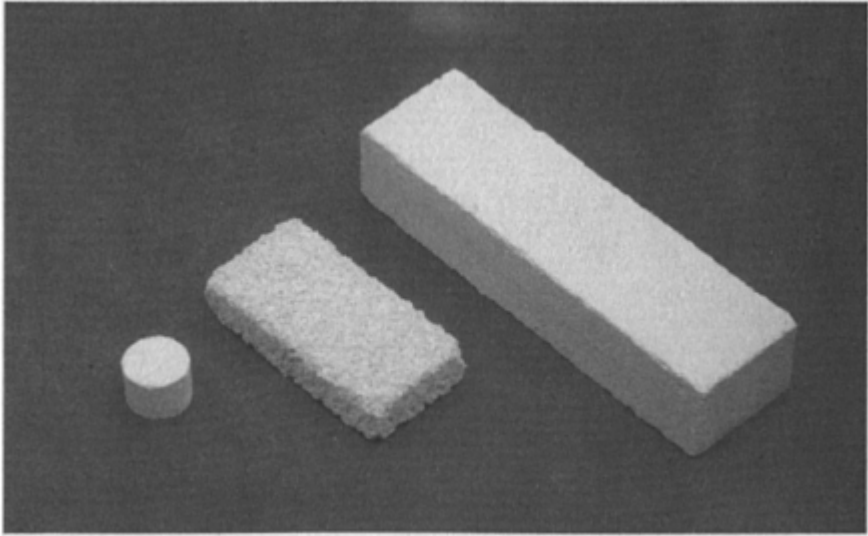


FIGURE 2.3 These samples of tricalcium phosphate are good examples of a resorbable bioceramic. (Courtesy of DePuy Inc.)

pH environment. Bioglass is essentially a soda-lime-silica glass with a significant phosphorous oxide addition. A central focus of the Bioglass research has been a composition labeled 45S5 containing 45 wt%  $\text{SiO}_2$ , 24.5 wt%  $\text{CaO}$ , 24.5 wt%  $\text{Na}_2\text{O}$ , and 6 wt%  $\text{P}_2\text{O}_5$ , noticeably lower in silica and higher in lime and soda than conventional window and container glasses. This and related Bioglass materials continue to be actively studied. Their practical application in orthopaedics has been limited, largely due to the slow kinetics of surface reaction rates and the corresponding slow development of interfacial bond strength. Roughly 6 months are required before the interfacial strength approaches that provided by traditional *polymethylmethacrylate (PMMA)* cement after 10 minutes setting time. On the other hand, Bioglass and related materials have found wide uses in dentistry and ear surgeries. A more detailed discussion will be given in [Section 5.6](#).

The discussion of this section indicates that the three categories of bioceramics identified in [Table 2.1](#) were well established by the mid-1970's. Some of the more interesting recent developments in bioceramics will be discussed in [Chapter 6](#) in connection with applications in orthopaedic surgery, dentistry, and cancer treatment.

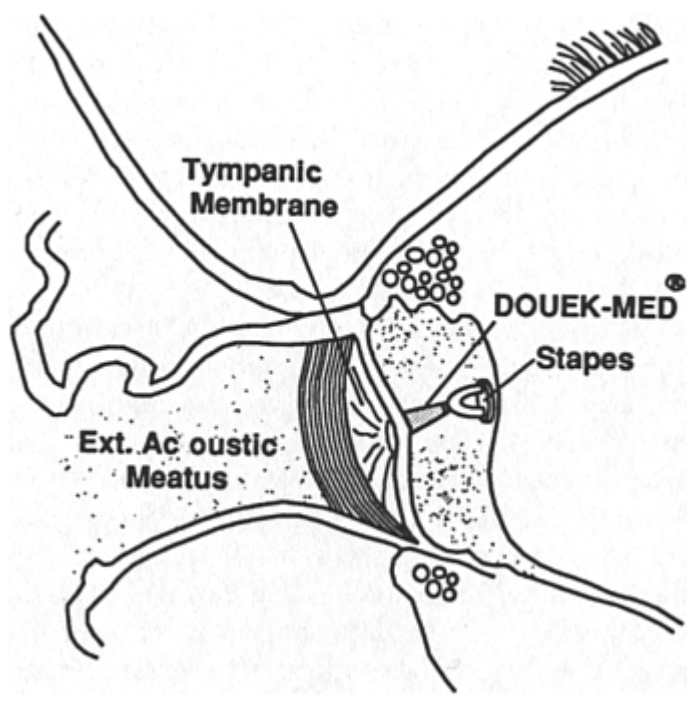


FIGURE 2.4 This piece of Bioglass (DOUEK-MED) serves as a sound-transmitting prosthesis between the ear drum (tympanic membrane) and the stapes footplate. (Courtesy of L.L.Hench)

## CHAPTER 3

### *Properties of Biomaterials*

Much of the understanding of *materials selection* for either industrial or biomedical applications centers on an appreciation of the basic properties of the materials under consideration. Before discussing bioceramics in detail, a brief definition of various material *properties* will be provided in this chapter. Much of this discussion is condensed from a broader introduction to the properties of engineered materials (Shackelford 1996).

#### 3.1

#### STRESS VERSUS STRAIN

A simple *tensile test*, as illustrated in [Figure 3.1](#), provides the most basic information about the mechanical behavior of a material. Specifically, this test indicates the strength of the material and the extent to which it can be deformed. The general result of a complete tensile test is a *stress-versus-strain curve*. An example for a typical industrial alloy (aluminum 2024-T81) is given in [Figure 3.2](#).

The axes in [Figure 3.2](#) represent the *engineering stress*,  $\sigma$ , and *engineering strain*,  $\epsilon$ , defined as

$$\sigma = P/A_0 \quad (\text{Eq. 3.1})$$

and

$$\epsilon = (l - l_0)/l_0 = \Delta l/l_0 \quad (\text{Eq. 3.2})$$

where  $P$  is the load on the sample with an original (zero-stress) cross-sectional area,  $A_0$ ,  $l$  is the gage length at a given load, and  $l_0$  is the original (zero-stress) length. For metallic structural materials, the behavior shown by [Figure 3.2](#) is typical. There is an initial, linear portion of the stress-strain curve representing *elastic deformation*, which is temporary in nature and associated with the stretching of atomic bonds between adjacent atoms in the alloy. Elastic deformation is followed by plastic deformation, which is permanent in nature and associated with the distortion and reformation of atomic bonds. Beyond the elastic limit of the alloy, atomic planes slide past each other in response to the increased level of engineering stress.

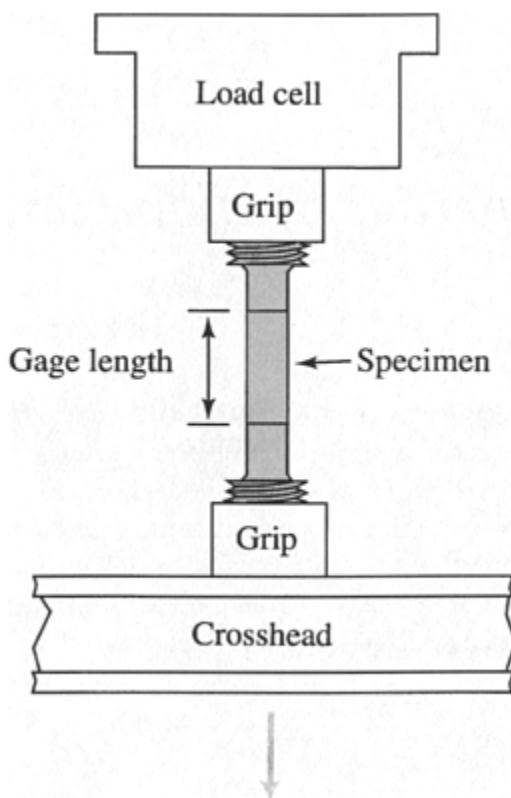


FIGURE 3.1 Schematic illustration of the tensile test. (After Shackelford 1996)

There are four key mechanical properties defined by the stress-strain curve. Figure 3.3 summarizes these properties. The slope of the stress-strain curve in the elastic region is the *modulus of elasticity*,  $E$ , which represents the stiffness of the material, that is, its resistance to elastic strain. The *yield strength*,  $Y.S.$ , is the stress necessary to generate a small amount (0.2%) of permanent deformation representative of the boundary between the elastic and plastic regions. The plastic deformation continues at stresses above the yield strength, rising toward a maximum called the ultimate tensile strength, or simply the *tensile strength*,  $T.S.$  Between  $Y.S.$  and  $T.S.$ , *strain hardening* of the alloy occurs. Beyond  $T.S.$ , the apparent drop in strength is simply the result of the “necking down” of alloy within the gage length. The engineering stress, as defined by Equation 3.1, decreases because the denominator,  $A_0$ , is larger than the actual area. The true stress ( $=P/A_{\text{actual}}$ ) would continue to rise to the point of fracture.

The complexity of the final stages of the necking down process causes the value of the failure stress to vary substantially from specimen to specimen. The strain at failure is a more useful property. *Ductility* can be defined as the percent elongation at failure ( $=100 \times \text{failure}$ ). Figure 3.3 also shows the definition of

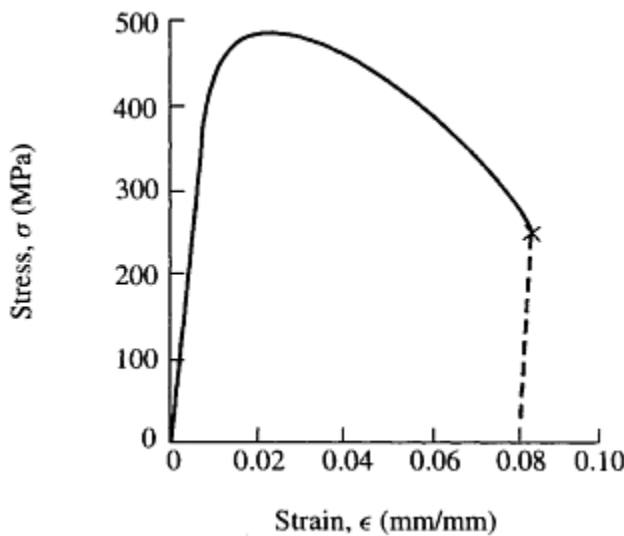


FIGURE 3.2 Typical result of a tensile test for a metallic specimen. This stress-versus-strain curve was obtained for an aluminum alloy. (After Shackelford 1996)  
toughness as the area under the stress-strain curve. As integrated - data are not routinely available, the toughness is not generally tabulated.

Although metal alloys typically display a substantial amount of plastic deformation (Figure 3.2), structural ceramics generally do not. Brittle fracture following the linear, elastic deformation region is characteristic of ceramics. Figure 3.4 summarizes this case for aluminum oxide. It is important to note that this typical ceramic is substantially weaker in tension than in compression. As a practical matter, this phenomenon is the result of small cracks produced during manufacturing which serve as “stress concentrators” under tensile loading. The mechanical performance of ceramics and polymers is frequently measured in a bending test (Figure 3.5), and strength is given by the *flexural strength*, also known as the *modulus of rupture (MOR)*.

Representative data for various natural and engineered materials are given in Table 3.1.

### 3.2 FRACTURE TOUGHNESS

As noted in the discussion relative to Figure 3.4, flaws such as microcracks can play a critical role in the mechanical behavior

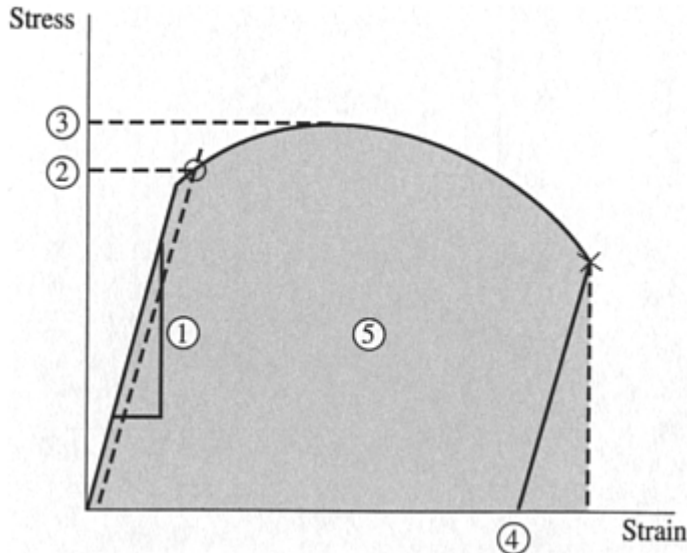


FIGURE 3.3 The key mechanical properties obtained from a tensile test are: 1) *modulus of elasticity, E*; 2) *yield strength, Y.S.*; 3) *tensile strength, T.S.*; 4) *ductility*, defined as  $100 \times \frac{\text{failure strain}}{\text{original length}}$ , and 5) *toughness*, defined as the area under the stress-versus-strain curve. Note that elastic recovery occurs after fracture (hence the sloped line above 4), while toughness is measured under load (hence the vertical dashed line). (After Shackelford 1996)

TABLE 3.1 Typical data from tensile and bending tests

Material	E (GPa)	Y.S. (MPa)	T.S. (MPa)	MOR (MPa)	$100 \times \epsilon_f$ (%)
Ti-6Al-4V	110	825	895	—	10
Dental gold alloy	—	—	310–380	—	20–35
Alumina crystal	380	—	—	340–1000	—
Sintered alumina ( 5% porosity)	370	—	—	210–340	—
Polyethylene (ultra-high molecular weight)	0.50	—	35	—	350
Bone	20	—	150	—	1.5
Collagen (tendon)	1.3	—	75	—	9.0

of materials. The science of *fracture mechanics* has emerged as the general analysis of the failure of structural materials with preexisting flaws. The most widely used single parameter from fracture mechanics is the *fracture toughness*,  $K_{IC}$  (pronounced “kay-one-see”) which is the critical value of the stress-intensity factor at a crack tip necessary to produce catastrophic failure under simple uniaxial loading. The subscript “I” stands for the “mode I” (uniaxial) loading



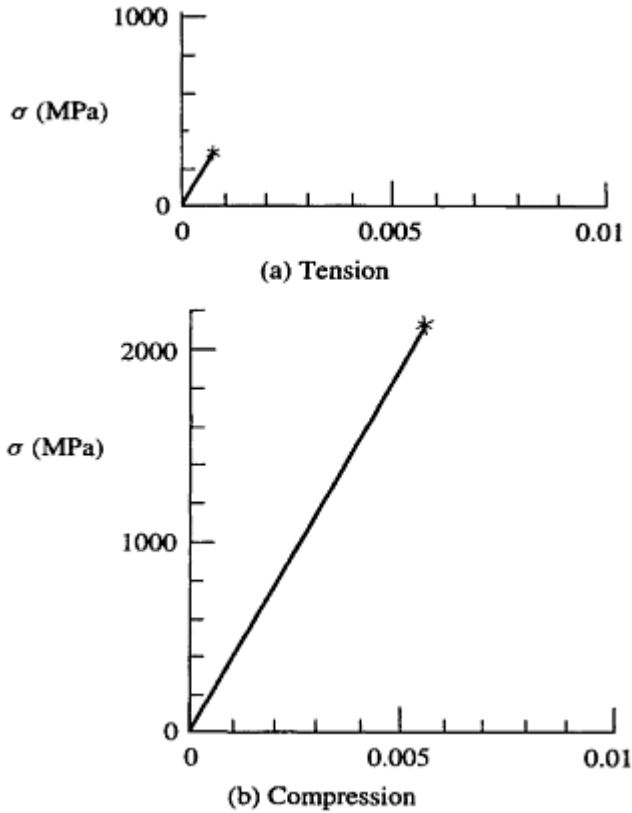


FIGURE 3.4 In contrast to the stress-versus-strain behavior of metals, as illustrated in Figure 3.2, only linear, elastic deformation is seen in the typically brittle fracture of a structural ceramic. Also characteristic of ceramics, this dense, polycrystalline alumina is (a) relatively weak in tension and (b) relatively strong in compression. (After Shackelford 1996)

illustrated in Figure 3.6. The subscript “C” stands for “critical.” In general, the fracture toughness is given by

$$K_{IC} = \sigma_f (\pi a)^{1/2} \quad (\text{EQ. 3.3})$$

where  $\sigma_f$  is the overall applied stress at failure, and  $a$  is the length of a surface crack (or one-half the length of an internal crack), as illustrated in Figure 3.6. As indicated by Equation 3.3, the units of fracture toughness are  $\text{MPa} \cdot \text{m}^{1/2}$ .

Table 3.2 gives the values of fracture toughness for a variety of engineered materials. Highly brittle materials, with little ability to deform plastically in the vicinity of a crack tip, have characteristically low values of  $K_{IC}$  and are susceptible to catastrophic failures. By contrast, highly ductile alloys can undergo

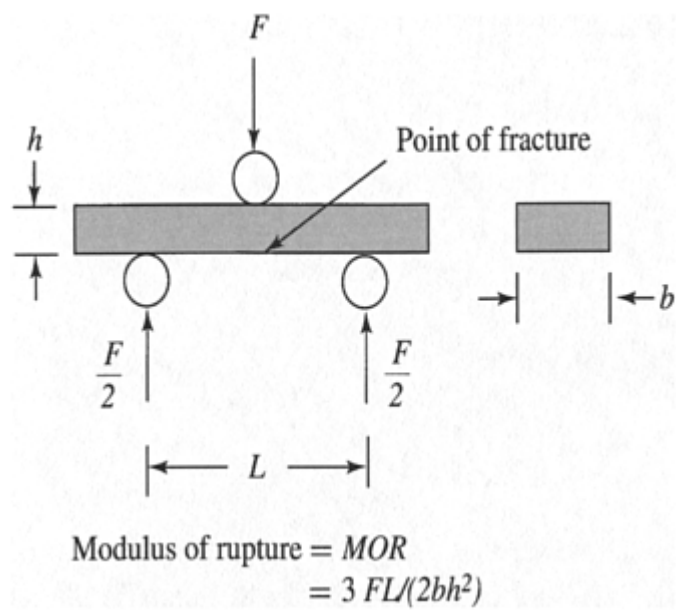


FIGURE 3.5 Schematic illustration of a bending test and the definition of the resulting *modulus of rupture*, also known as the *flexural strength*. (After Shackelford 1996)

TABLE 3.2 Typical fracture toughness data

Material	$K_{IC}$ (MPa · m <sup>1/2</sup> )
Ti–6Al–4V	55–115
Pressure vessel steels	170
Aluminum alloys (high to low strength)	23–45
Sintered alumina	3–5
Partially stabilized zirconia	9
Silicate glass	<1
High-density polyethylene	2

substantial plastic deformation at the crack tip and will tend to fail only after substantial, overall plastic deformation.

3.3  
FRICTION AND WEAR

*Friction* is the resistance to motion when a solid object is moved (or attempted to be moved) tangentially with respect to the surface of another solid (Rabinowicz 1995). It is estimated that 0.5% of the Gross National Product of industrialized countries is lost due to the failure to minimize frictional losses during sliding. At

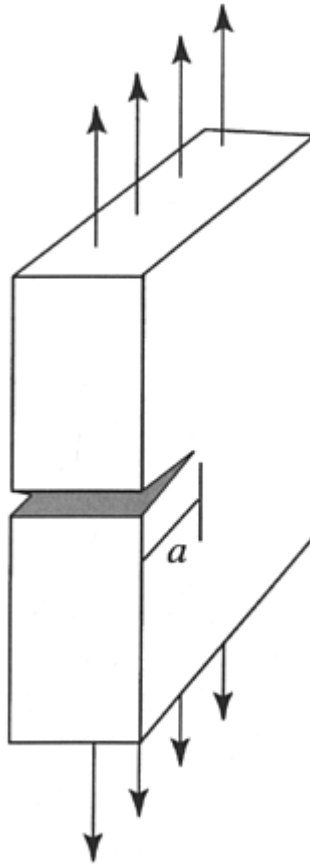


FIGURE 3.6 Schematic illustration of the fracture toughness test. (After Shackelford 1996)

the same time, some minimal level of friction is required in many everyday processes, such as walking and driving a car.

In general, one can define a *coefficient of friction*,  $\mu$ , as the proportionality constant between a friction force,  $F$ , attempting to move an object along a surface and the normal force on the object,  $L$ :

$$F = \mu L \quad (\text{Eq. 3.4})$$

The normal force will be the combination of resolved components of its weight and any forces acting on the object. As it is well known that the friction force to start sliding is generally greater than the force to maintain sliding, the coefficient of friction is normally tabulated as “static” (for surfaces at rest) and “kinetic” (for surfaces in motion relative to each other). On closer inspection, however, the static coefficient of friction is seen to be a function of time of contact, and the

kinetic coefficient of friction is a function of the relative velocity of the two surfaces.

*Wear* can be defined as the physical degradation of a material. More specifically, it is the removal of surface material as a result of mechanical action. The amount of wear debris need not be large in order to be devastating to the engineering or biomedical application. The failure of an automobile engine with inadequate lubrication or the loss of function in a total hip prosthesis due to wear debris are important examples.

Four main forms of wear have been identified: (1) *Adhesive wear* occurs when two smooth surfaces slide over each other and fragments are pulled off one surface and adhere to the other. The strong bonding or “adhesive” forces between adjacent surfaces give rise to the name for this category. (2) *Abrasive wear* occurs when a rough, hard surface slides on a softer surface. The softer surface becomes grooved, resulting in the formation of wear particles. (3) *Surface fatigue wear* occurs during repeated sliding or rolling over a track. Surface or subsurface crack formation leads to the breakup of the surface. (4) *Corrosive wear* accompanies sliding in a chemically corrosive environment. As will be discussed in the next section, corrosion protection often depends on the formation of a protective, “passive” surface layer. Mechanical sliding action can break down passivation layers helping to maintain a high corrosion rate.

Nonmetallic materials are well known for superior wear resistance. High-hardness ceramics generally provide excellent resistance to wear. Aluminum oxide and partially stabilized zirconia are good examples. Polytetrafluoroethylene (PTFE) is an example of self-lubricating polymer that is widely used for its wear resistance.

### 3.4 CORROSION

*Corrosion* can be defined as the chemical degradation of a material. It is generally identified with the dissolution of a metal into an aqueous environment, which is an electrochemical process. The chemical reaction of nonmetallic materials with their environment, however, does not generally involve an electrical current but is nonetheless sometimes referred to as “corrosion.” These nonmetallic materials are generally rather inert in comparison to metals, and we shall focus on the more traditional definition of corrosion in regard to metallic materials.

A classic example of corrosion is given in [Figure 3.7](#), which illustrates a *galvanic cell*. The chemical change (such as the corrosion of the anodic iron) is accompanied by an electrical current. The driving force for the overall cell is the relative tendency for each metal to ionize. Because of the common occurrence of galvanic cells between dissimilar metals, a systematic collection of half-cell reactions can be tabulated and is known as an *electromotive force (emf) series*. “Active” metals such as sodium and magnesium tend to be anodic in the

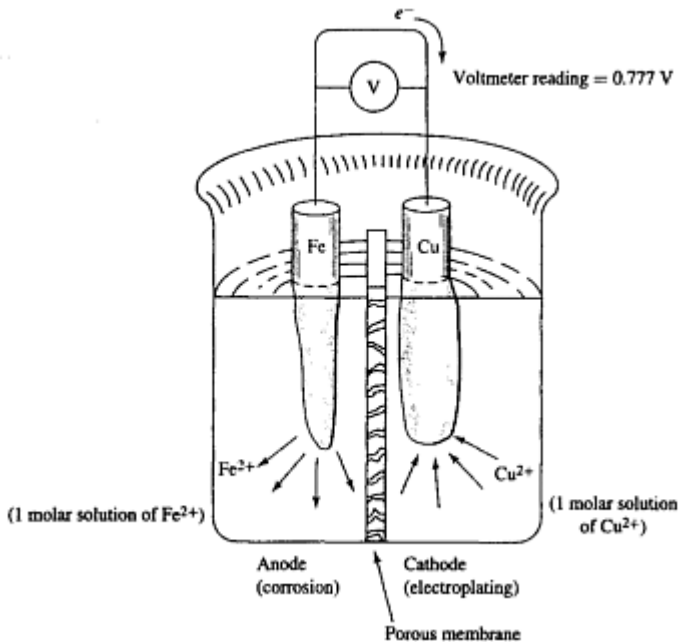


FIGURE 3.7 Schematic illustration of *corrosion* in a *galvanic cell*, in which the corrosive degradation of iron is seen to be part of an electrochemical process involving the dissimilar metal copper. (After Shackelford 1996)

presence of “noble” metals such as gold and platinum which tend to be cathodic. Of greater engineering significance is an empirical tabulation of commercial alloys, ranked by their relative activity in a given aqueous environment. This *galvanic series* can be a useful guide to alloy selection.

Dissimilar metals are only one type of corrosion source. Different levels of ionic concentration can lead to corrosion. A region of lower concentration is anodic and corroded relative to a higher concentration region. This electrochemical cell is appropriately termed a *concentration cell*. Similarly, an *oxygen concentration cell* can be formed when a low concentration of dissolved, gaseous oxygen is present on the surface of a metal part. Restricted areas such as surface cracks and threaded fit tings are common examples. Regions of high mechanical stress, such as cold-worked areas and grain boundaries, also tend to be anodic. These *stress cells* are susceptible to local corrosive attack.

Ceramic and glass coatings on metals can provide a protective barrier to the environment and subsequent *corrosion prevention*. A more subtle coating is provided by the “passivation” of a metal surface by the formation of a thin, oxide coating. The stable (Fe, Cr) oxide coating on stainless steel is a classic example.

### 3.5 BIOCOMPATIBILITY

As we have seen to this point, identifying a material for a biomedical application requires more than verifying adequate mechanical properties. We must also be concerned about the material's resistance to mechanical and chemical degradation (wear and corrosion). Beyond those traditional engineering issues, however, applications in biomedicine have the additional requirement of *biocompatibility*, i.e., long term physiologic compatibility (Martin 1996a). Ordinarily, an implant is expected to function for many years. Changes which occur in and around the implant must not be physiologically harmful. The biomaterial should either release no toxic ions or release them gradually, or those ions should not accumulate to the point that they would produce an immunological response. From a biomechanical perspective, an implant should not perturb the stress distribution in adjacent tissues to the extent that normal tissue remodeling is prevented.

To appreciate the challenges of biocompatibility, one must recall that living organisms have evolved with the one over-riding principle of survival. As a result, all organisms seek to prevent the invasion of foreign matter. The organism will generally attempt to destroy the invader at the molecular level or to encapsulate with an impenetrable, cellular wall. Overcoming the body's resistance by destroying the body's defenses (the immune system) is a dangerous strategy. More practical is to choose an implant material which is "invisible" to the body's chemical sensors. Better yet is to find a material that is "attractive" to the physiology of the body. The recent success of hydroxyapatite implant materials is due to its similarity to bone mineral and the resulting integration with bone when implanted in the skeleton.

## CHAPTER 4

### *Related Biological Materials*

Certain natural, *biological materials* have a significant relationship to engineered ceramics used in biomedicine. In this Chapter, these will be described in terms of either their inherent similarity to ceramics or their relationship to an implanted bioceramic.

#### 4.1

##### HYDROXYAPATITE

*Hydroxyapatite*,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , is the primary mineral content of bone and calcified cartilage, representing 43% by weight of bone (Martin, 1996b). It has the desirable physiochemical attributes of stability, inertness, and biocompatibility. The elastic modulus of hydroxyapatite is two orders of magnitude greater than that of collagen, the primary polymeric component of bone to be described in the next section of this chapter.

It should also be noted that the mineralization of vertebrate skeletons is due to structural requirements. The mineral content of bone is much greater than needed as a physiologic reservoir. As the density of hydroxyapatite is about three times greater than most other biological materials, there is a significant metabolic cost in using this natural ceramic.

A microscopic image of a hydroxyapatite is shown in [Figure 4.1](#). This microradiograph shows bone (gray) grown into a porous coralline hydroxyapatite material (white) 16 weeks after implantation. This image is the result of a preliminary evaluation of a bioceramic of the type to be discussed in more detail in [Section 6.1.3](#) in conjunction with defect and fracture repair.

#### 4.2

##### COLLAGEN

*Collagen* is a natural, polymeric protein and the most important structural material in vertebrates (Martin 1996b). Collagen constitutes 36% of bone by weight, the second largest component after hydroxyapatite. The form of collagen found in bone is termed Type I and is the dominant form throughout the body, being found in tendons, ligaments, and skin. A bundle of collagen fibers adjacent

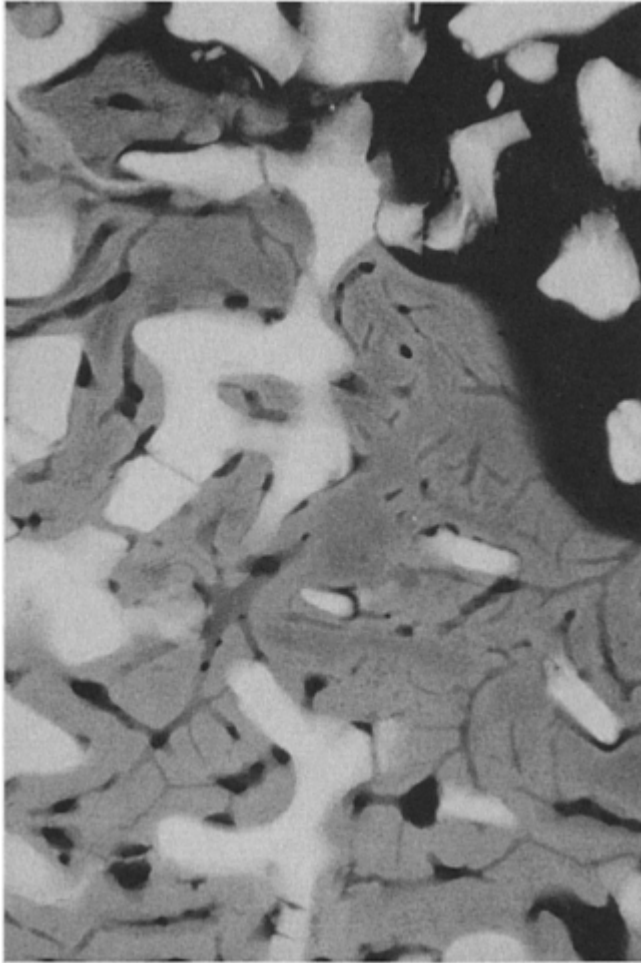


FIGURE 4.1 Microradiograph of bone (gray) grown into a porous coralline hydroxyapatite material (white) 16 weeks after implantation. (Courtesy of R. Bruce Martin)

to a bioceramic implant surface is shown in [Figure 4.2](#). Collagen contains three tropocollagen molecules with left-handed spiral structures in turn wound into a right-handed superhelix. The more than a dozen types of collagen are distinguished by variations in the patterns of amino acids in their polymeric chains.

Molecular cross-linking is common and can be intramolecular between two of the three polypeptides in a single molecule or intermolecular. Precise fiber alignment is necessary to facilitate intermolecular cross-linking, leading to a characteristic banding structure with a 6.4 nm repeat dimension. An abundance of cross-linking in tendons and ligaments leads to relatively rigid mechanical



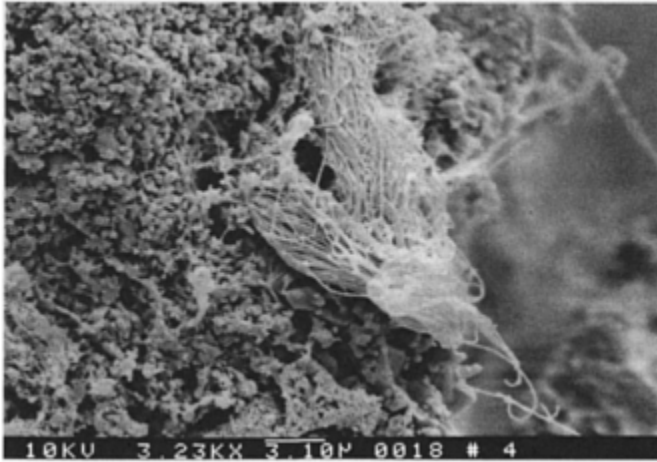


FIGURE 4.2 A scanning electron micrograph of ordered collagen fibers laid down in direct contact with granules of a bioceramic implant material. (After McIntyre, et al. 1991)

behavior. Skin, on the other hand, is highly visco-elastic with rubber-like mechanical behavior. Figure 4.3 shows the contrasting stress-strain behavior for these various systems. Obviously, the maximum elastic modulus of collagen (as indicated by tendons) is about 1,000 MPa and the maximum strain is 10-20%. It is interesting to note that the aging of skin is the result of continuing cross-linking leading to reduced deformability or “stretch.”

### 4.3 DENTIN

The inner portion of a tooth is composed of *dentin* (Martin 1996b). It is more highly mineralized than bone, with approximately 80% hydroxyapatite in an organic matrix which accounts for the remaining 20%. Approximately 90% of the matrix is collagen. Because of the high concentration of hydroxyapatite, dentin is a relatively brittle material.

### 4.4 CHITIN

After collagen, *chitin* is the second most common component of connective tissues in animals (Martin 1996b). Chitin is chemically similar to cellulose and has a lamellar structure similar to wood or bone. Its elastic modulus is close to that of hardwoods and bone, and it tends to be mixed with protein for the purpose of adjusting its mechanical properties to the specific structural need. Its mineral content is aragonite (orthorhombic  $\text{CaCO}_3$ ), rather than hydroxyapatite. This biological material is named after the Chiton, a genus of mollusks having a

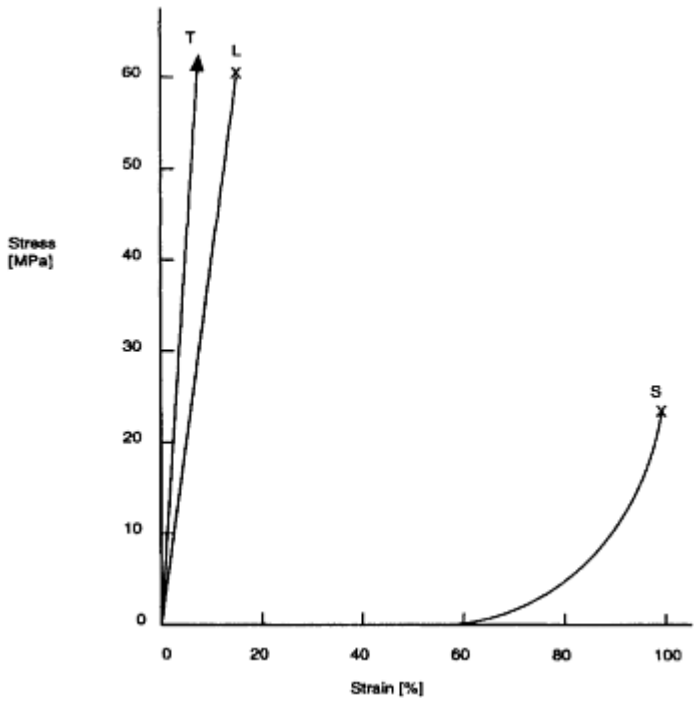


FIGURE 4.3 The comparative stress-versus-strain curves of tendon (T), ligament (L), and skin (S). (After R.B.Martin 1996b)

chitinous dorsal plate. In general, chitin is found in many invertebrates, especially in the insect exoskeleton (cuticle).

## CHAPTER 5

### *Bioceramics—Classified by Composition*

*Bioceramics* can be conveniently classified by their primary chemical constituents. Some are composed of relatively simple oxides, while others are relatively complex chemically. Microstructural features are also a factor, e.g., in the glass-ceramics and ceramic-matrix composites.

#### 5.1 Al<sub>2</sub>O<sub>3</sub>-BASED CERAMICS

As indicated in [Chapter 2](#), simple oxides were a primary focus of the development of modern bioceramics in the late 1960's (Hulbert et al. 1982-83). The development of dense, high-purity (>99.5%) Al<sub>2</sub>O<sub>3</sub> structural ceramics by sophisticated sintering technology was well established by that point, and Al<sub>2</sub>O<sub>3</sub> was the first bioceramic widely used clinically. (Hench 1993).

Alumina ceramics are used for orthopaedic surgery as hip prostheses and in dentistry as dental implants. Their widespread use is based on a combination of good strength, modest fracture toughness, high wear resistance, good biocompatibility and excellent corrosion resistance. In addition to the polycrystalline, sintered aluminas, some dental implants have been fabricated from single-crystal sapphire.

To ensure maximum strength and fracture toughness, materials processing is critical. It is desirable to maintain an average grain size less than 4 μm and a chemical purity greater than 99.7%. Similarly, the extremely low coefficient of friction and wear rate for alumina is dependent on a small grain size combined with a narrow grain-size distribution.

The inherently high level of chemical inertness is, of course, intimately associated with the successful performance of alumina in regard to corrosion resistance and biocompatibility. Experience with alumina in orthopaedic surgery for more than twenty years demonstrates its high degree of biocompatibility. More specifically, alumina is associated with minimal scar formation. As will be seen in [Chapter 6](#), scar formation prevents the mechanical bonding of bone to a porous implant surface.

The specifics of hip replacement surgery will be described in [Chapter 6](#). In essence, the natural ball-and-socket geometry of the hip is replaced by synthetic

materials. In Europe, both the ball and socket are often fabricated of alumina. This design is stimulated by the exceptionally low friction and wear of the alumina-on-alumina system. To properly utilize these properties, the ball and socket must have a high degree of sphericity which is produced by grinding and polishing the mating surfaces together. The wear rate in this system can be ten times lower than that of the conventional metal alloy ball against a polymeric socket.

Although well-engineered alumina/alumina ball-and-socket systems in Europe have demonstrated long-term performance, the lack of the highest quality control standards can lead to severe problems with wear debris damage. In the United States, hip prosthesis designs are largely confined to the use of alumina for the ball, with the socket being made from ultra high molecular weight polyethylene (UHMWPE).

In dentistry, alumina has been used in various dental implants, including blade, screw, and post configurations. Alumina has also been used in jaw bone reconstruction.

Other clinical applications of alumina include knee prostheses, bone segment replacements, bone screws, middle ear bone substitutes, and corneal replacements.

## 5.2

### ZrO<sub>2</sub>-BASED CERAMICS

Zirconia, ZrO<sub>2</sub>, has become a popular alternative to alumina as a structural ceramic because of its substantially higher fracture toughness (Shackelford 1996). Zirconia, in fact, has the largest value fracture toughness of any monolithic ceramic. Static and fatigue strengths for zirconia femoral heads have been found to exceed clinical requirements, but a primary reason for this application has been the decreased factional torque and the reduced level of polyethylene debris production (Kumar et al. 1991). The wear performance has been shown to be superior even to alumina which in turn is superior to that of metal alloys. An additional factor in this wear resistance is that the zirconia/polyethylene interface has a low coefficient of friction, reducing the level of torque to the polyethylene socket and thereby reducing the incidence of loosening.

In addition, zirconia heads, because of their low modulus and high strength, can be manufactured in a greater range of sizes and neck lengths. On the other hand, the success of the attachment of the ceramic ball onto the metal alloy stem is critically dependent on the mating of the surfaces and the quality of their surface finishes. Stress raisers (high points on the conical stem) must be avoided to prevent fracture of the ceramic head at extremely low loads.

It is also worth noting that the low wear rate of both alumina and zirconia in comparison to metal alloy heads produces negligibly small amounts of metal ion release. In wear tests which produced over 100 ppb levels of metal ion release

using cobaltchrome or Ti-6Al-4V alloys, ceramic heads were found to have less than 5 ppb, the experimental detection limit (Davidson and Kovacs n.d.).

### 5.3

#### OTHER SIMPLE OXIDES

A variety of simple ceramic oxides were used in the pioneering studies of bioceramics in the late 1960's and early 1970's. For example, Hulbert, et al. (1972) evaluated  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ ,  $\text{CaO} \cdot \text{TiO}_2$ , and  $\text{CaO} \cdot \text{ZrO}_2$  as both porous and non-porous implants in rabbit muscles and connective tissue for up to 9 months. Although such studies proved to be reasonably successful and helped to establish the basic understanding of the utility of ceramics in biomedicine and the role of porosity in their function, simple alumina ceramics generally performed better in implantation studies (Hulbert et al. 1982–83). By the end of the 1970's, alumina had become the bioceramic of choice based on its combination of biocompatibility and strength. Later, the development of relatively high-fracture toughness zirconia ceramics led to their consideration as an alternative to alumina. Both alumina and zirconia are discussed in detail in the previous two sections of this chapter.

### 5.4

#### HYDROXYAPATITE

It is ironic that such an obvious candidate as *hydroxyapatite* did not come into fashion as a biomaterial for many years. As noted in [Chapter 3](#), hydroxyapatite,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , is the primary mineral content of bone representing 43% by weight. It has the distinct physiochemical advantages of stability, inertness, and biocompatibility. The relatively low strength and toughness of hydroxyapatite, however, produced little interest among researchers when the focus of attention was on bulk structural samples. The now widespread and successful application of hydroxyapatite has largely been in a thin-film configuration. The thin, surface-reactive coating has been applied to a variety of prosthetic implants, primarily for total hip replacement (de Lange and Donath 1989). These coatings have been plasma-sprayed on both Co-Cr and Ti-6Al-4V alloys. Optimal performance has come from coating thicknesses on the order of 25–30 micrometers. Interfacial strengths between the implant and bone are as much as 5 to 7 times as great as with the uncoated specimens. The enhanced interfacial development corresponds to the mineralization of bone directly onto the hydroxyapatite surface with no signs of intermediate, fibrous tissue layers. The substantial success of this coating system has led to its widespread use in total hip replacement prostheses. An example of an HA coated hip prosthesis is shown in [Figure 5.1](#).

Another successful application of a hydroxy apatite-containing biomaterial is a novel composite system composed of a biphasic ceramic (hydroxyapatite plus tricalcium phosphate) and collagen, the polymeric form of protein which

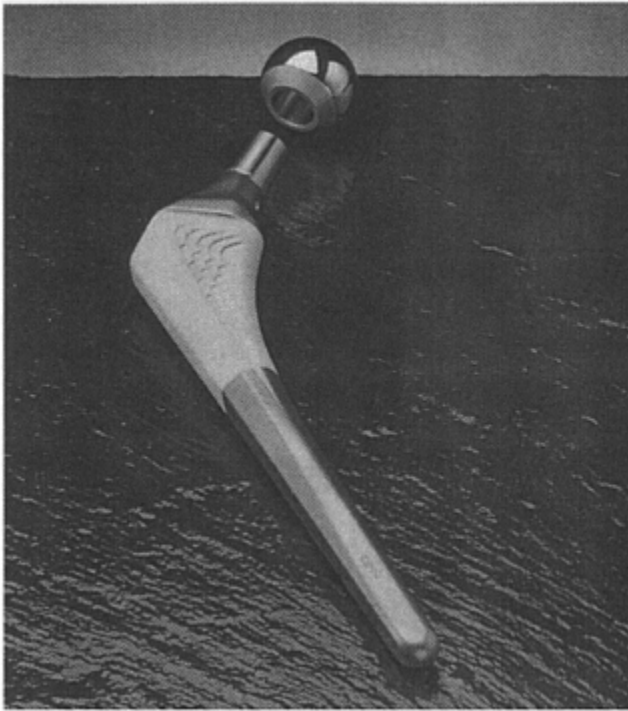


FIGURE 5.1 The upper third of the femoral stem in this hip prosthesis is coated with hydroxyapatite for the purpose of improved adhesion between the prosthesis and bone, in which hydroxyapatite is the predominant mineral phase. (Courtesy of Osteonics)

constitutes about 36% by weight of natural bone (McIntyre et al. 1991). This bone-like composite has been the focus of substantial research and development by Professor Michael Chapman and co-workers at the University of California-Davis. An even more bone-like form is produced by the addition of bone marrow taken from the test animal. It should be noted that this biocomposite is not a ceramic-matrix composite. The collagen is the matrix phase containing mm-scale particles of the biphasic ceramic. The biphasic ceramic was produced by Zimmer Corporation from a high-purity, tribasic calcium phosphate powder. The material was sintered for 4 hours at 1050°C and crushed to approximately 1 mm-size granules composed of approximately 40% beta-TCP and 60% HA with substantial microporosity (less than one micrometer) but little macroporosity (greater than 100 micrometers). Implant specimens were prepared by mixing the coarse ceramic granules into a matrix of bovine fibrillar type I collagen manufactured by Collagen Corporation. (This type of collagen is widely used in dermatologic and plastic surgical applications.) The ceramic phase was 36% by weight and approximately 20% by volume of the (HA/TCP)/collagen composite. In some specimens, autogenous bone marrow was obtained from the test animal

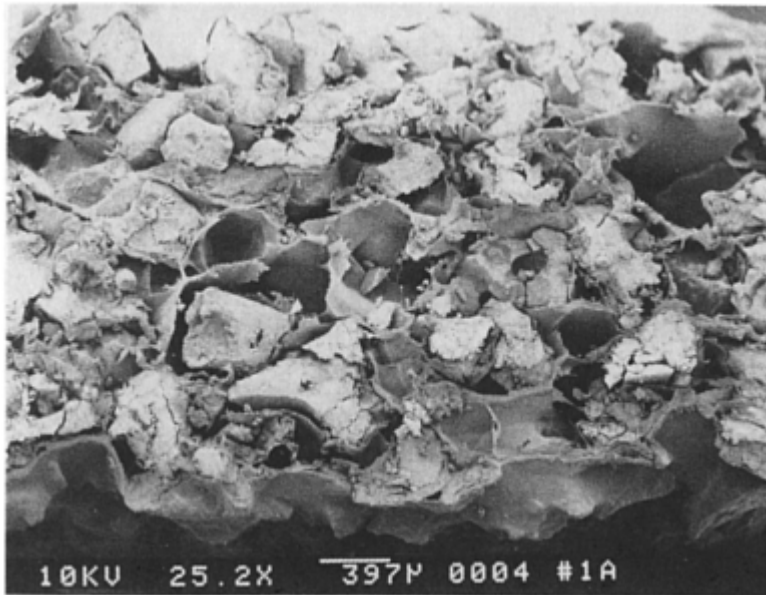


FIGURE 5.2 Low magnification view of the interior of a collagen-matrix composite block. The collagen provides a smooth coating for the irregular ceramic granules (composed of hydroxyapatite and tricalcium phosphate). In addition, the 100  $\mu\text{m}$  scale interstices among the granules allow for bone tissue ingrowth, although they are filled with collagen before implantation. (After McIntyre, et al. 1991)

and added as 20 volume % of the overall composite system (reducing the overall ceramic component to 16% by volume). Scanning electron microscopy of the unimplanted ceramic/collagen composite indicated that the collagen matrix is indirectly responsible for providing the macroporosity which allows the bone ingrowth comparable to that discussed previously for cementless THR fixation. The collagen matrix also provides a mechanical cushion for the sharp-edged ceramic granules. (See [Figure 5.2](#))

During the materials development phase, composite specimens were implanted into 25 mm defects in the forelimbs of several adult dogs. Ceramic composites, both with and without bone marrow additions, showed excellent results providing complete union as demonstrated by radiographic inspection and good mechanical integrity as indicated by post-implantation torque tests. Scanning electron microscopy of the explanted specimens indicated extensive infiltration of new bone trabeculae directly onto the ceramic, as well as the resorption of TCP particles. (See [Figure 5.3](#)) In addition, there was microscopic evidence of new, ordered fibrous collagen formation, along with good vascularization (the formation of healthy red blood cells and blood vessels). The success of the laboratory evaluation led to the use of the ceramic-containing composite system in clinical studies, and, now a commercial product, *Collagraft*, is available from Zimmer Corporation. The final *Collagraft* product uses a slightly higher HA/TCP ratio of 65/35.

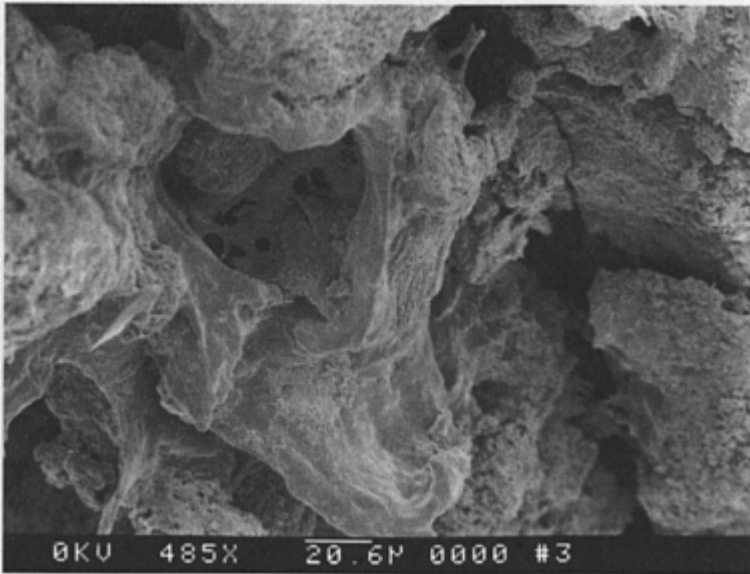


FIGURE 5.3 A scanning electron micrograph of new bone that has been laid down directly on the bioceramic composite. (After McIntyre, et al. 1991)

## 5.5

### OTHER CALCIUM SALTS

In [Chapter 2](#), we noted that the successful use of *tricalcium phosphate* (TCP), with the chemical formula  $\text{Ca}_3(\text{PO}_4)_2$ , as a bioceramic as early as 1920 (Albee and Morrison 1920). It was also noted that in numerous studies on calcium hydroxide, this ceramic salt tended to stimulate the formation of immature bone and was an example of an unsuccessful bioceramic (Hulbert et al. 1982–83). Today, TCP remains as a useful bioceramic and a good example of the “resorbable” category of bioceramics. The use of TCP in conjunction with hydroxyapatite (HA) is described in the previous section and in [Section 6.1.3](#).

## 5.6

### SILICATE CERAMICS AND GLASSES

*Silicates* represent the dominant category of the traditional ceramics and glass industries (Shackelford 1996). These materials are economical due to the abundant availability of raw materials. Also, silicates provide adequate mechanical, thermal, and optical properties for a wide range of traditional and advanced materials applications. The specialized requirements of biomedical applications, however, make silicates less significant as bioceramics. One should recall that ceramics and glasses are distinguished primarily by the presence



respectively of crystalline or noncrystalline structure on the atomic-scale. For crystalline silicate ceramics, biomedical applications have been relatively negligible. For noncrystalline silicate glass, biomedical applications have been more significant because of the development of *Bioglass*, the classic example of the “surface reactive” category of bioceramics as pointed out in [Chapter 2](#).

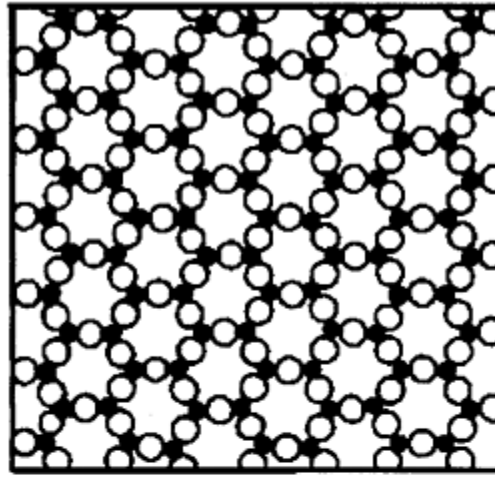
Bioglass can be called a “bioactive” material. It has been shown to bond to bone, and specialized compositions can even bond to soft tissues. These bioactive materials typically undergo a surface modification upon implantation, forming a biologically active hydroxycarbonate apatite (HCA) layer which provides the bonding interface with the tissues. The comparable chemical structure in HCA and the mineral phase of bone accounts for the tendency for interfacial bonding in that case.

The bonded interface provides substantial strength. Often, the interfacial strength is greater than the cohesive strength of either the adjacent ceramic or tissue. As noted in [Chapter 2](#), many bioactive silica glasses have been based on a composition labeled 45 S5 containing 45 wt%  $\text{SiO}_2$ , 24.5 wt%  $\text{CaO}$ , 24.5 wt%  $\text{Na}_2\text{O}$ , and 6 wt%  $\text{P}_2\text{O}_5$ , noticeably lower in silica and higher in lime and soda than conventional window and container glasses. Also distinctive in comparison to traditional silicate glasses is the significant phosphate component,  $\text{P}_2\text{O}_5$ , which plays a critical role in the bioactivity. Hench (1993) and co-workers have determined that a molar ratio of at least 5:1  $\text{CaO} : \text{P}_2\text{O}_5$  is desirable to ensure that the Bioglass surface bonds to bone. In general, biologically active glasses contain less than 60 mol%  $\text{SiO}_2$ , relatively high  $\text{Na}_2\text{O}$  and  $\text{CaO}$  contents, and a  $\text{CaO}:\text{P}_2\text{O}_5$  ratio greater than 5:1.

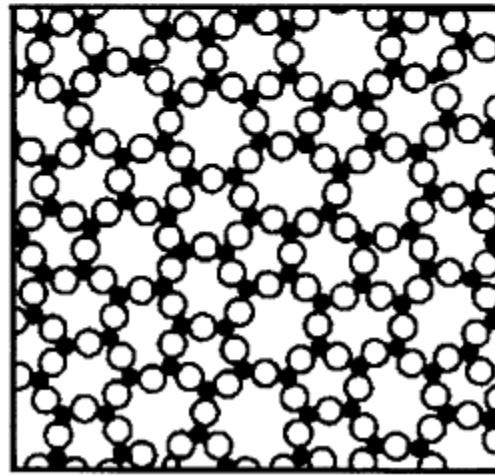
Bioglass implants based on the 45S5 composition have been successfully applied in a variety of dental and medical applications. For example, certain ear bones have been replaced, and, for denture wearers, the 45S5 material has been used to maintain the jawbone for up to 8 years, with a nearly 90% retention rate. Also, it has been used to restore the bone next to teeth that might otherwise be lost to gum disease.

## 5.7 GLASS-CERAMICS

As noted in the previous section, we distinguish chemically similar materials as “ceramics” and “glasses” by the presence or absence, respectively, of crystallinity ([Figure 5.4](#)). A sophisticated form of crystalline ceramics are the “glass-ceramics,” which are first produced like ordinary glassware and are then transformed into crystalline ceramics by a careful heat treatment. The advantage of the initial, glass stage is that the product can be formed into a complex shape economically and precisely by conventional glass-forming technology. The advantage of the subsequent crystallization is that the final microstructure is fine-grained with little or no residual porosity. Such a microstructure tends to provide optimal mechanical performance in a ceramic. Glass-ceramic products typically



(a)



(b)

FIGURE 5.4 Two-dimensional schematic comparing (a) a crystalline and (b) a noncrystalline oxide. The noncrystalline material retains short-range order (the triangularly coordinated building block) but loses long-range order (crystallinity). Part (b) serves to define the term “glass.” (After Shackelford 1996)

have good resistance to mechanical shock due to the elimination of stress-concentrating pores. It should be noted that the crystallization process is not always 100% complete, but that the residual glass phase effectively fills the grain boundary volume, helping to create the pore-free structure (Figure 5.5).



FIGURE 5.5 A replica micrograph of the fracture surface of a glass-ceramic, indicating an essentially pore-free structure. (After L.R.Pinckney in *Engineered Materials Handbook, Vol. 4, Ceramics and Glasses*, ASM International, Materials Park, OH, 1991, p. 437.)

Conventional glass ceramics are based on composition systems such as  $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ , which produce crystalline phases with exceptionally low thermal expansion coefficients and subsequent resistance to thermal shock. An additional, critical component of the composition of conventional glass ceramics is the addition of a few mol% of a nucleating agent such as  $\text{TiO}_2$  which facilitates the characteristic, fine-grained crystalline microstructure.

Glass-ceramics for biomedical applications are more typically based on compositions similar to the Bioglass system. Conveniently,  $\text{P}_2\text{O}_5$  serves as a nucleating agent in the same way as  $\text{TiO}_2$ . Low-alkali (0 to 5 wt%) silica glass-ceramics, known as *Ceravital*, have been successfully used for more than a

decade as implants in middle-ear surgery to replace bone damaged by chronic infection (Hench 1993). In Japan, a two-phase silica-phosphate glass-ceramic has been developed. Known as A/W glass-ceramic, it consists of an apatite phase,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH}_1\text{F}_2)$ , a wollastonite phase, and a residual glassy matrix. A/W glass-ceramic has been used successfully in hundreds of patients for replacing part of the pelvic bone and in vertebral surgery. An easy-to-machine silica-phosphate glass-ceramic has been developed in Germany, which contains phlogopite (a type of mica) and apatite crystals.

Finally, it should be noted that compositional ranges in which bioglasses and bioglass-ceramics bond effectively with bone and other tissues is generally limited. For example, small additions of certain oxide components such as  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  can inhibit bone bonding in these systems.

5.8  
CERAMIC-MATRIX COMPOSITES

As noted in Section 5.2, zirconia ceramics are increasingly popular alternatives to alumina ceramics because of their relatively high fracture toughness values. *Ceramic-matrix composites* (CMC's) are proving to have even higher values of fracture toughness, comparable to that in some common structural metal alloys. (See Table 5.1) In CMC's, micromechanical mechanisms,

TABLE 5.1 Comparison of ceramic matrix composites (CMC's) fracture toughness values with data from Table 2.1

Material	$K_{IC}$ (MPa · m <sup>1/2</sup> )
CMC's	
SiC whiskers in $\text{Al}_2\text{O}_3$	8.7
SiC fibers in SiC	25.0
SiC whiskers in reaction-bonded $\text{Si}_3\text{N}_4$	20.0
Other materials	
Ti-6Al-4V	55-115
Pressure vessel steels	170
Aluminum alloys (high to low strength)	23-45
Sintered alumina	3-5
Partially stabilized zirconia	9
Silicate glass	<1
High-density polyethylene	2

such as the pull-out of reinforcing fibers from the matrix, cause crack growth to be retarded and the fracture toughness to be subsequently higher.

As with silicate ceramics and glasses, the more common CMC's used in industry are not necessarily appropriate for biomedical applications. In addition

to the advantage of improved fracture toughness, design goals in developing CMC's for biomedicine have focused on increasing flexural strength and strain to failure, while decreasing elastic modulus (Hench 1993). A good example is an A/W glass-ceramic containing a dispersion of tetragonal zirconia which has a bend strength of 703 MPa and a fracture toughness of 4 MPa.m<sup>1/2</sup>.

## CHAPTER 6

### *Bioceramics—Classified by Application*

*Bioceramics* have found a wide range of applications in medicine, especially in recent years. In this chapter, we shall focus on three broad fields, viz. orthopaedics, dentistry, and cancer treatment.

#### 6.1 ORTHOPAEDICS

Within orthopaedics, our primary focus will be total hip replacement (THR) surgery. The potential for ceramic material applications in THR will be explored, along with the implications of new technologies in THR surgery. The recent development of robotic surgery is an important example. Other joint replacements will also be reviewed. The most detailed discussions will involve the recent applications of hydroxyapatite. This ceramic mineral which comprises nearly half of natural bone is showing great promise as a coating for THR prostheses and as a primary component in various materials being used to repair large bone defects.

##### 6.1.1 Total Hip Replacement

The total hip replacement (THR) is a highly successful and widely used example of contemporary orthopaedic surgery (Chapman 1993). More than 200,000 THR surgeries are performed in the United States each year, with a similar number in Europe. The THR was developed in England by the surgeon, Sir John Charnley, who was knighted for this achievement. The essence of Charnley's invention was to provide adequate fixation for the artificial prosthesis which is used to replace the natural ball-and-socket of the hip joint. Following the surgical removal of the defective ball-and-socket (often defective due to degenerative arthritis), a metallic femoral stem was placed into an opening drilled into the medullary canal of the femur. Stainless steel was the original alloy used for the stem and the attached ball. The artificial cup for the acetabular side of the joint (in the hipbone) was fabricated of ultrahigh molecular weight polyethylene. The primary contribution by Charnley was to adapt the use of

*polymethylmethacrylate (PMMA)* cement from dentistry to fix the femoral stem and acetabular cup. Subsequent design development has led to cementless alternatives to the use of PMMA. [Figure 6.1](#) summarizes the total hip replacement surgery. As with the development of bioceramics, the materials selection for the THR was reasonably well established by the mid-1970's (Fraker and Ruff 1977). [Table 6.1](#) summarizes the most common materials-of-choice for contemporary THR surgeries. Only in the past decade has a ceramic material, *hydroxy apatite* for the cementless design, appeared on this list.

Other than the hydroxyapatite coating on certain cementless designs, the artificial hip joint is typically a metal/polymer system. Stainless steel has largely been replaced by cobalt-chrome alloys (for cemented implants) and Ti-6Al-4V alloy (for cementless implants). The titanium alloy is undesirable for the cemented design due to its lower elastic modulus which leads to an excessive load on the interfacial cement. The original cementless design involved a porous surface for tissue bone ingrowth, comparable to the philosophy used by Hulbert and co-workers on the early inert oxide bioceramics (Hulbert et al. 1970; Hulbert 1969; Talbert 1969; Klawitter 1970).

More than two decades of research on bioceramics led to the appearance of an engineering ceramic on the list of [Table 6.1](#). As

TABLE 6.1 Current engineered materials for the total hip replacement (THR)

Component	Material
Femoral Stem	Co-Cr alloys or Ti-6Al-4V
Ball	Co-Cr alloys
Acetabular Cup	Ultrahigh molecular weight polyethylene (UHMWPE)
Cement	Polymethylmethacrylate (PMMA)
Cementless	Porous surface coating or hydroxyapatite coating

noted in [Section 5.4](#), hydroxyapatite coatings do not have to be porous in order to provide strong bonding to bone. These plasma-sprayed coatings exhibit enhanced interfacial strength due to the mineralization of bone directly onto the hydroxy apatite surface.

In addition to noting the widespread use of hydroxyapatite, consideration of other ceramic material substitutions can be a useful exercise. [Table 6.2](#) provides a list of potential ceramic substitutions for some of the traditional materials of [Table 6.1](#).

The most difficult substitution would be a replacement for the metallic femoral stem. Obvious candidates would be those ad

TABLE 6.2 Current and potential engineered ceramics for the total hip replacement

Component	Material
Femoral Stem	Partially-stabilized zirconia (PSZ)

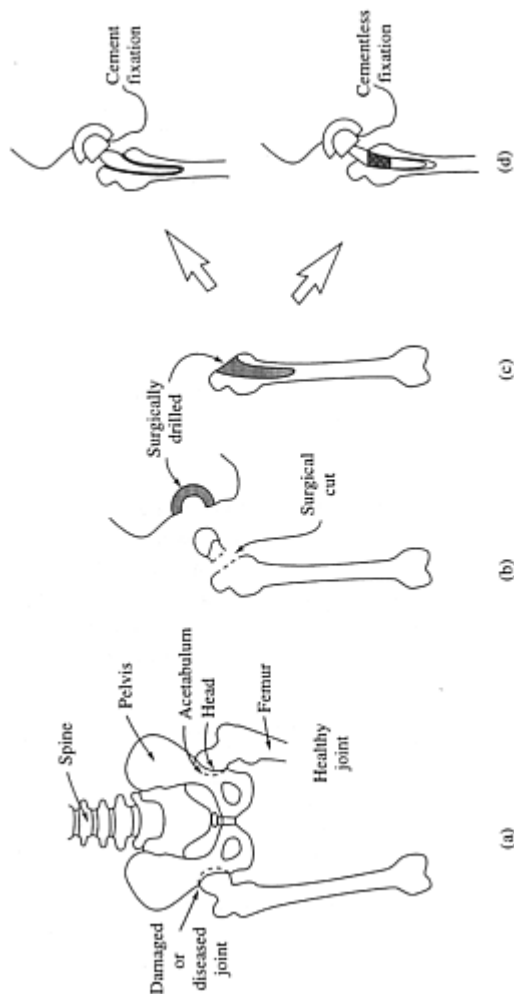


FIGURE 6.1 Schematic illustration of the total hip replacement (THR) surgery. For typical cementless fixation, the upper one-third of the femoral stem is either covered with a porous metal coating or, more recently, with a thin layer of hydroxyapatite. (After Shackelford 1996)

Component	Material
	or
	Ceramic-matrix-composites
Femoral Ball	Al <sub>2</sub> O <sub>3</sub> or PSZ
Acetabular Cup	Al <sub>2</sub> O <sub>3</sub> or PSZ
Cement	–
Cementless	Hydroxyapatite



vanced structural ceramics, such as partially-stabilized zirconia or various ceramic matrix composites, which would have superior values of fracture toughness. As a practical matter, polymer matrix composites are more probable competitors for femoral stem applications (Hunt 1987).

The compressive load on the femoral ball makes any high density structural ceramic, such as  $\text{Al}_2\text{O}_3$ , a good candidate for that application. In Sections 5.1 and 5.2, we saw that, at least in Europe, alumina and zirconia ceramics have been used extensively for this purpose. An especially attractive feature of ceramics for femoral heads is the typically low surface wear of structural ceramics. In a similar way, the acetabular cup can be fabricated from  $\text{Al}_2\text{O}_3$  or PSZ. The low toughness of these structural ceramics, however, has contributed to a continued dominance by polyethylene. The PMMA cement for fixation does not have a serious ceramic competitor.

One must also be aware of the materials implications of new orthopaedic surgical technologies. An important example is the recent development of robotic surgery (Paul et al. 1994). (See Figure 6.2) The initial demonstration of feasibility for this technique was made at the University of California-Davis using an image-driven machining tool for total hip replacement in the dog. In essence, the robotic machining operation replaces the traditional surgical procedure in which the openings for the femoral stem and acetabular cup were made by hand-held surgical tools. There are dramatic advantages to the robotic procedure. The femoral cavity cross-section is oversized (compared to the prosthetic stem) by less than 1 % using the robot, compared to over 30% for typical human surgical technique. The average gap between the stem and bone cavity is 0.05 mm for the robotic technique, compared to 1.2 mm for the human effort. These improvements in “fill” and “fit” of the THR prosthesis lead to a total of more than 95% direct contact between the cross-sectional perimeter of the prosthesis and bone for the robotic surgery, compared to only 20% for the human surgery. This creates an ideal situation for the cementless THR design. (The increasing role of hydroxyapatite coatings is obviously related to this area.) Finally, one should note that robotic THR increases the need for improvements in the area of materials evaluation, specifically the use of computerized-axial tomography (CAT) scans to optimize the robotic machining. The result will be the potential for an increased level of customizing of the THR prostheses.

### 6.1.2

#### Other Joint Replacement

As seen in the previous section, hip joint replacement has become a highly popular and successful surgery. Orthopaedic surgeons have appropriately looked at other joints for similar replacement strategies (Chapman 1993). In some cases, a design philosophy similar to the total hip replacement is used. In others, somewhat different approaches are required.



FIGURE 6.2 Robotic surgery is an advance in orthopaedics. The use of computer-controlled machining technology in creating the opening for the femoral stem leads to a substantially improved fit between the prosthesis and the bone. (Courtesy of Robodoc—Integrated Surgical Systems) (See [Color Plate I](#))

A popular generalization about joint replacement surgeries is that the difficulty of the surgery increases as one moves radially away from the hip joint. Closest to the hip, the knee has been the joint which has benefited most from the technology of the THR surgery. Knee replacement surgery is now widely practiced in the United States. Most prostheses are similar to THR's in materials selection, with a femoral component made of either cobalt-chrome or titanium alloys and a high-density polyethylene (HDPE) for the wear surface connected to the tibia bone. The tibial HDPE component often has a metal backing. A unique feature of the knee prosthesis is the need for a patella (knee cap), which is also made of HDPE but without a metal backing. A high frequency of patella failures was

observed when a metallic component was included. Because of the different geometry of the knee replacement in comparison to the THR, there is not particular advantage of cobalt-chrome versus titanium alloy for the femoral component. The trade-off between the use of PMMA cement versus cementless fixation is similar to that for the THR, although the knee prosthesis is less forgiving to loosening due to the prosthesis being on the ends of the femur and tibia bones rather than inserted down a long femoral shaft. Once surgeons mastered the art of prosthesis alignment, cement fixation proved to be essentially as successful as cementless. One can assume that hydroxyapatite coatings for prosthesis fixation will have substantial promise in knee replacement surgery as it has in THR's, although HA applications in hip surgery are much more widely used at this point in time.

The total shoulder replacement also involves a design similar to the THR, with a metal alloy "head" attached to a stem which is implanted into the humerus bone. The metal head mates to a HDPE "glenoid" which is sometimes metal-backed. Elbow reconstruction surgery involves a significantly different design. Rather than a metal/polymer sliding joint, the elbow prosthesis is a coupled axle design joining the humerus and ulna bones. This complex design is susceptible to complications of motion loss and infection. Total ankle replacement is an especially challenging surgery. The complex biomechanics of the ankle limit replacement surgery to elderly, sedentary patients or patients with systemic arthritis. For young, heavy, or active patients, ankle fusion is more practical. In the more limited and experimental surgeries for shoulder, elbow, and ankle replacement, ceramic applications are not expected to provide a serious challenge in the near future to the common use of metals and polymers.

### 6.1.3

#### Defect and Fracture Repair

Large *bone defects* can be defined as centimeter-scale gaps in the skeletal system. Historically, such defects have been repaired by harvesting bone from another part of the body (autogenous bone grafting or "*autografts*" ) or using cadaver bone ("*allografts*" ) . The harvest of an autogenous bone graft carries significant morbidity and cost which makes an off-the-shelf synthetic bone attractive (Younger and Chapman 1989). Allografts have problems with immunologic reaction and the risk of acquiring diseases transmissible by tissues and fluids. These limitations and concerns created substantial interest in the development of materials as bone graft substitutes or extenders. A pioneering example of hydroxyapatite and tricalcium phosphate for the repair of large bone defects was outlined in [Section 5.4](#) and is described in greater detail by McIntyre, et al. (1991). In [Section 4.1](#) an alternative material was introduced, viz., a so-called "coralline hydroxyapatite." It was manufactured from coral by a thermochemical process which converts the calcium carbonate manufactured by the marine organism to a calcium phosphate (hydroxyapatite). As seen in [Figures 2.2](#) and [4.1](#), an attractive

feature of using the coral-route is that it has an open porous structure which is ideal for accommodating bone ingrowth.

Another recent development for bone repair utilizes a novel in situ ceramic processing technique (Constantz et al. 1995). The hydroxyapatite (HA) formed by conventional ceramic processing techniques tends to be more dense, coarse-grained, and less fatigue-resistant than HA formed *in vivo*. A more natural HA can be produced by the surgical implantation of a paste that hardens in minutes under physiological conditions. The paste is produced by adding a sodium phosphate solution to a mixture of monocalcium phosphate monohydrate [MCPM,  $\text{CaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ ],  $\alpha$ -tricalcium phosphate [TCP,  $\text{Ca}_3(\text{PO}_4)_2$ ] and calcium carbonate (CC,  $\text{CaCO}_3$ ). The paste is injectable for about 5 minutes and maintains physiologic temperature and pH. The injected paste hardens due to the crystallization of dahllite within about 10 minutes. Dahllite is a carbonated hydroxyapatite. The specific formula for the crystallized paste in this system is  $\text{Ca}_{8.8}(\text{HPO}_4)_{0.7}(\text{PO}_4)_{4.5}(\text{CO}_3)_{0.2}(\text{OH})_{1.3}$ , which would indicate some substitution by acidic phosphate,  $(\text{HPO}_4^{2-})$ . The paste's initial compressive strength is 10 MPa, and, within 12 hours, the conversion to dahllite is about 90% complete giving a final compressive strength of 55 MPa, a value greater than that of cancellous bone. The final tensile strength is 2.1 MPa, a value about the same as that for cancellous bone. The average grain size for the crystallized paste is 20–50 nm, comparable to that in natural bone.

Using this surgical paste which hardens in situ, fractured bones can be held in place while natural bone remodeling occurs, replacing the implant with living bone and creating an implant-bone composite. The progressive replacement of the dahllite implant by living bone can result in an increasingly durable skeletal segment. This bioceramic is marketed under the name *Norian SRS* (for "skeletal repair system"). This system mimics the mineralization process of coral, which involves physiochemically controlled reactions. The actual mineralization of bone involves protein-directed reactions, a process that has eluded synthetic imitation. Both narrow fractures and large defects can be filled by this system. This bioceramic may be especially well suited to repair mechanically compromised osteoporotic bone.

Finally, it is worthwhile to review the status of bioceramics for defect repair following substantial clinical experience in recent years. A recent, comprehensive study sponsored by the Department of Veterans Affairs provided an interesting comparison of a variety of commercially available ceramics as bone graft substitutes (Johnson et al. 1996). Within the limitations mentioned earlier for autogenous bone grafts, cancellous (or spongy) bone harvested from the patient's iliac crest can be taken as an effective standard for comparison with candidate synthetic materials. This study compared three commercially available granular ceramic materials: a coralline-based hydroxyapatite (Interpore International, Irvine, CA), a  $\alpha$ -tricalcium phosphate (DePuy, Warsaw, IN), and the biphasic ceramic/collagen composite introduced in Section 5.4 (Zimmer, Warsaw, IN). Evaluations were based on the performance of the ceramic in

repairing a 25 mm defect in a canine radius bone, in comparison to the performance of a cancellous bone autograft in the opposite leg of the same dog. All three ceramic samples were tested with and without the addition of bone marrow. The study found that HA and TCP alone are unsuitable substitutes. On the other hand, the addition of bone marrow made these ceramics comparable in performance to the cancellous bone graft after six months of implantation. It appears that cells provided by the bone marrow are responsible for imparting the stimulation of bone growth at the ceramic surface within the first month of implantation. The ceramic/collagen composite demonstrated competitive performance with or without bone marrow addition, although the performance may be maximized by additional marrow. It appears that collagen may facilitate bone formation by serving as a requisite to forming endochondral bone (i.e., the “long bones” of the skeleton). The authors of the study, however, preferred TCP with bone marrow to the ceramic/collagen material because HA, unlike TCP, is not readily resorbed by the body and is more opaque radiographically than TCP making radiographic evaluation of the degree of healing and bone formation difficult. For this reason, the authors suggest that an “ideal” graft material might be TCP plus collagen and bone marrow.

Figure 6.3 illustrates how a typical bioceramic for defect repair is prepared for surgery. Shown are strips of *Collagraft* (HA/TCP ceramic granules in a matrix of collagen). The tray in which the strips are packaged contains a compartment in



FIGURE 6.3 The preparation of bioceramic strips for the surgical repair of bone defects. (Courtesy of Zimmer) (See [Color Plate II](#) )

which the strips are hydrated with sterile saline and coated with bone marrow. The strips may be used as is or molded into another desired shape.

Defect and fracture repair promises to be one of the most dynamic areas of bioceramic application in the near future, as reflected in research that is *not* concentrating on load-bearing ability (a weakness for ceramics) but the ceramic's role as a delivery system for bone morphogenetic proteins (BMP). The actual mineralization of bone involves protein-directed reactions, a process that is only recently being controlled clinically. As noted above, bone marrow is routinely used with materials such as *Collagraft* for stimulating bone growth. A more sophisticated approach, however, is the use of BMP (Reddi 1997). The therapeutic effectiveness of these BMP for bone regeneration is now well established. It is also accepted that the clinical effectiveness can be enhanced by a delivery system. Of the various delivery systems considered to date, a leading candidate is porous hydroxyapatite (Ohgushi, et al., 1997).

## 6.2 DENTISTRY

A wide variety of ceramics, glasses, and glass-ceramics have been used in dental applications. (Hench 1993; Clark and Anusavice 1991; Day 1995). The relatively smaller scale and primarily compressive loads have combined to make

applications in dentistry less challenging than in orthopaedic surgery. Examples include dental implants, cementation agents, and restorative materials.

### 6.2.1

#### Traditional Porcelains

*Dental porcelains* have been used for nearly two centuries to repair diseased and decayed teeth (Day 1995). Approximately 80% of all fixed prostheses placed in the United States are composed of porcelain-fused-to-metal. Today, porcelains are also used for the cosmetic treatment of broken or discolored teeth. Veneers can be cemented to front teeth, and bridges can be used to replace lost teeth. Three-tooth bridges are fabricated by fusing the porcelain to a metal substrate.

Dental porcelains are generally made by blending two components, typically a partially fused potassium aluminosilicate feldspar (leucite) and a fully fused alkali—alkaline-earth—aluminosilicate. Leucite is added to raise the thermal expansion coefficient of the system to more closely match that of the metallic alloy substrate (in prosthodontic devices such as crowns and bridges). The second, glassy component controls the melting characteristics of the mixture. Additives produce the desired optical properties, including color and fluorescence. A typical metal substrate would be an 80Ni-20Cr alloy. Good adhesion of the porcelain depends on good thermal expansion matching as well as a preoxidation step to produce a monolayer of  $\text{Cr}_2\text{O}_3$  to ensure good oxide adherence and overall strength.

### 6.2.2

#### Other Ceramics for Dental Reconstruction

As pointed out in [Section 5.1](#), alumina ceramics have been used in dental applications. Relatively pure alumina, including the single crystal sapphire form, has been used as dental implants, as well as in jaw bone reconstruction.

An alternative to traditional dental porcelains are glass-ceramic prosthetics, which offer many benefits including ease of fabrication, low processing shrinkage, high strength, translucency control, insensitivity to abrasion damage, thermal shock resistance, chemical durability, and polishability. (Clark and Anusavice, 1991) [Figure 6.4](#) shows an example with the commercial name Dicor (Dentsply International, York, PA). This glass-ceramic system is based on the growth of fluorine-containing, tetrasilic mica crystals. The addition of up to 7 wt.% zirconia is believed to improve chemical durability and enhance translucency. This glass-ceramic is stained on the external surface with a shading porcelain to achieve acceptable aesthetics. [Figure 6.4](#) shows the resulting color match of a shade guide tab relative to the maxillary central incisors.

As pointed out in [Section 5.5](#), some of the primary applications of *Bioglass* implants have been in the dental field (Day 1995). Bioglass has been implanted in the jaw bone to fill the cavity caused by removal of teeth due to disease or

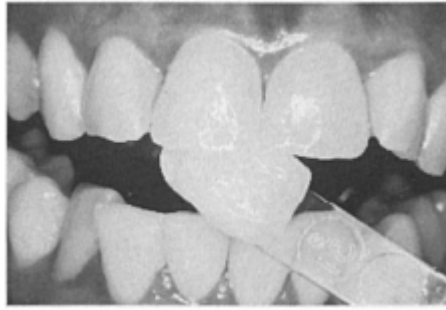


FIGURE 6.4 Color match of a glass-ceramic crown for the maxillary central incisors. (Courtesy of David Grossman) (See [Color Plate III](#))

injury. Filling this cavity is important to prevent change in jawbone shape over time and the subsequent difficulty for the person to wear dentures. Well over 90% of such implants are successful five years beyond implantation, compared with losses greater than 50% for implants made from other materials. Another application is in the repair of teeth with periodontal disease. In this case, crushed Bioglass particles (90 to 700  $\mu\text{m}$ ) are mixed with saline and placed around the tooth to stimulate bone growth. Thousands of patients worldwide are treated in this manner.

Dental cements are composed of a variety of complex chemical systems (Clark and Anusavice 1991). Many of these involve ceramic components. Often the cement functions by a mechanism of mechanical locking, rather than true chemical adhesion. A good example is the system involving a zinc phosphate matrix. Zinc oxide is the main powder constituent, and phosphoric acid is the liquid component. This system is also used as a “base,” in which a large amount of tooth structure has been removed and the ceramic is placed next to the pulp tissues, shielding them from the dental amalgam. The ceramic base serves the critical function of thermal insulation.

A steadily increasing use of resin-composites has occurred since they were introduced to dentistry in the early 1960's (Clark and Anusavice 1991). These systems consist of an organic polymer (resin) matrix, a ceramic filler, and a coupling agent (binder) between the two components. The most common resin is aromatic dememacrylate monomer, bisphenol A-glycidyl methacrylate (BIS-GMA). The ceramic filler is typically quartz, colloidal silica, or silicate glasses containing strontium or barium. The coupling agent used to coat the filler particles is a silane. Resin-composites have been used extensively to repair and rebuild teeth. The popularity of the resin-composites is based on their more desirable aesthetics compared to metal amalgams. In addition, there is a growing concern about the potential danger of mercury in traditional metal amalgams, and the resin-composites are prime candidates for substitution in that regard. Resin-composites, however, have not been widely used for posterior restorations.



Aesthetics considerations are not so significant for those “back teeth,” and the resin-composites demonstrate inferior wear and failure performance.

### 6.3 TREATMENT OF CANCEROUS TUMORS

In the past decade, two separate bioceramic systems have proven useful for the treatment of cancer. Each uses a distinct mechanism. The first to be described involves the internal delivery of therapeutic radiation using glass beads. The second involves a ferromagnetic glass-ceramic, which allows the thermal treatment of bone tumors locally.

#### 6.3.1 Glass Bead Delivery Systems

There are a number of advantages to *in situ* irradiation of internal organs in comparison to using external radiation sources (Day 1995). The radiation is applied in a more localized area. There is less damage to healthy tissue. Higher radiation doses can be applied for shorter periods of treatment and with less patient discomfort.

A potential method for *in situ* irradiation involves the dissolution of a  $\beta$ -emitting radioisotope in chemically insoluble glass microspheres (White and Day 1994). The glass microspheres must be biocompatible and nontoxic. In addition, they must be insoluble to ensure that the radioactive material is not released into the body. A more subtle criterion is that there must be no unwanted elements that would become radioactive after neutron bombardment. Finally, the microspheres must be sized to lodge in the capillary bed of the organ to be treated.

Yttria aluminosilicate (YAS) glasses can meet these criteria. Yttrium is the only element forming a radioactive isotope (Y-90) upon neutron bombardment. The absence of alkali ions gives the glass a high chemical durability. Glasses can be melted with as much as 50 wt% yttrium, allowing them to be highly radioactive and providing subsequent high doses for medical applications.

Preliminary clinical studies have been highly promising. Liver cancer patients have been given localized doses of  $\beta$ -radiation. This form of cancer is generally fatal independent of treatment. Applications of the *in situ* irradiations, however, have led to significantly longer survival times. Doses as high as 15,000 rads can be safely delivered by this technique. Also, there are minimum side effects, contributing to an improved quality of life for the patients. [Figure 6.5](#) illustrates the glass bead treatment system.



# CHAPTER 7

## *Biomimetic Materials*

Our closing chapter focuses on ways in which studies of biomaterials have led to new concepts for producing engineered materials. This fertile area of research and development is highly synergistic, as new materials produced in these novel ways which imitate natural, biological processes may prove to be superior candidates for biomedical applications.

### 7.1

#### MODEL, NATURAL FABRICATION PROCESSES

*Biomimetic processing* is a name given to fabrication strategies for ceramics that imitate certain natural processes such as the formation of sea shells (Shackelford 1996). This has been an outgrowth of a concentrated effort about two decades ago in the fabrication of ceramics and glasses by *sol-gel processing*. In this technique, the essential feature is the formation of an organometallic solution. The dispersed phase “sol” is then converted into a rigid “gel,” which, in turn, is reduced to a final composition by various heat treatments. A key advantage of the sol-gel process is that the product formed initially through this liquid phase route can be fired at substantially lower temperatures than required for conventional *firing* processes involving ceramic powders. There are significant cost savings from the lower firing temperatures.

Biomimetic processing takes the liquid phase processing route to its ultimate conclusion. As illustrated in [Figure 7.1](#), the formation of an abalone shell takes place in an aqueous medium entirely at ambient temperature, with no firing step at all (Heuer et al. 1992). Attractive features of this natural bioceramic, in addition to ambient processing conditions, are that the source materials are readily available and the final microstructure is fine-grained with an absence of porosity and microcracks. (See [Figure 7.2](#).) The fine microstructure produces a material (the abalone shell) with a relatively high strength and fracture toughness.

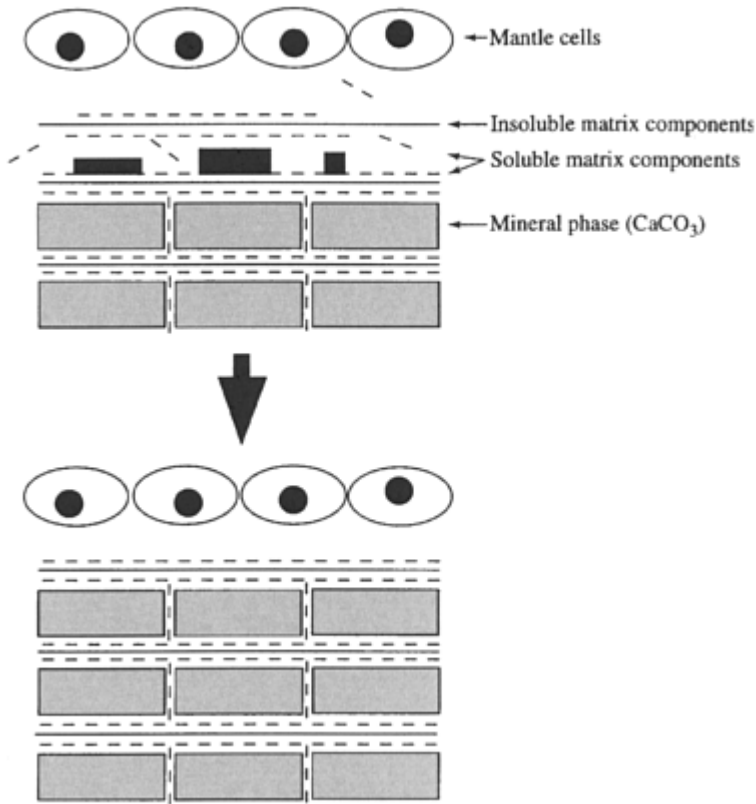


FIGURE 7.1 Schematic illustration of the formation of an abalone shell. A layer of nacre (composed of platelets of  $\text{CaCO}_3$  bonded together by various proteins and sugars) is shown. "Biomimetic processing" is the production of such fracture-resistant structures by synthetic means. (After Shackelford 1996)

## 7.2

### ADVANCED CERAMICS BY BIOMIMETIC PROCESSES

Biomimetic processing of engineering materials imitates the natural processes described in the previous section by the low-temperature aqueous syntheses of oxides, sulfides, and other ceramics by adapting certain biological principles (Heuer et al. 1992). The key aspects are: (1) the occurrence within specific microenvironments (implying stimulation of crystal production at certain functional sites and inhibition of the process at other sites), (2) the production of a specific mineral with a defined crystal size and orientation, and (3) macroscopic growth by packaging many incremental units together (resulting in a unique composite structure and accommodating later stages of growth and repair). This general process occurs for bone and dental enamel, as well as sea

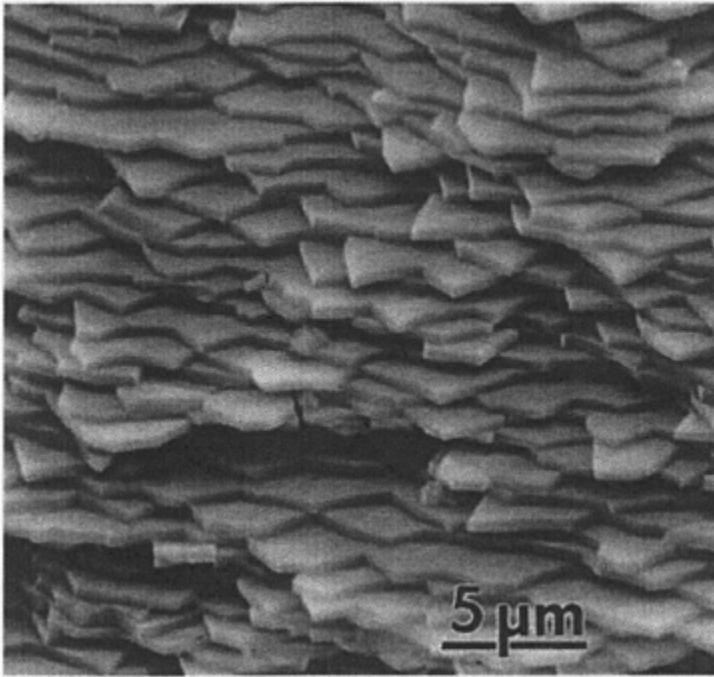


FIGURE 7.2 A scanning electron micrograph of the nacre platelet structure illustrated in Figure 7.1. (Courtesy of Mehmet Sarikaya)

shells, and consequently is of special interest in terms of producing materials for biomedical applications.

A simple example of biomimetic processing is the addition of water-soluble polymers to Portland cement mixes thereby reducing freeze-thaw damage by inhibiting the growth of large ice crystals. The ceramic-like cement particles resemble biological hard tissue. The polymer addition can change hardening reactions, microstructure, and properties of cement products in the same way that extracellular biopolymers contribute to the properties of bones and shells.

An additional, attractive feature of biomimetic processing is that it can represent *net-shape processing*, i.e., the product, once formed, does not require a final shaping operation. The form of teeth and sea shells are common examples. Biominerals are formed as relatively large, dense parts in a “moving front” process in which incremental matrix-defined units are sequentially mineralized. The resulting net-shape forming of a dense material represents an exceptional level of microstructural control.

A good example of biomimetic processing is a novel method for the production of ceramic thin films (Bunker et al. 1994). Precipitation from aqueous solution allows ceramic films to be applied on surfaces which are not amenable to conventional ceramic coating techniques. For example, ceramic coatings on

polymers can provide unique optical, magnetic, and physical properties. Processing temperatures greater than 300°C, however, pyrolyze most polymers, and many polymers will soften above 100°C. Even advanced sol-gel techniques involve heat-treating precursor films (usually alkoxides) at processing temperatures in excess of 400°C.

Biom mineralization is a complex process, but practical use of the technique can be made by concentrating on duplicating individual stages of an overall process. In this way, biomimetic processing has been used to create mineral coatings for industrial applications. High-quality, oriented, and patterned ceramic films can be deposited on polymers (and other materials) at temperatures below 100°C.

It is important to note that organisms are capable of controlling surface nucleation and growth on inert substrates. For example, macromolecules interact with the collagen matrix in eggshell membranes to induce or inhibit the crystallization of calcium carbonate or calcium phosphate during eggshell production. Tailored macromolecules in living organisms represent, then, a type of surface functionalization. Model surfaces can be formed by laying down self-assembled monolayers (SAM), as illustrated in [Figure 7.3](#). A typical species to form the monolayer is  $\text{Cl}_3\text{Si}(\text{CH}_2)_n\text{X}$ , where the chlorosilane end of the molecule,  $\text{Cl}_3\text{Si}$ , is covalently anchored to the substrate surface, the hydrocarbon chain,  $(\text{CH}_2)_n$ , provides for the “self-assembly” due to the van der Waals forces between adjacent molecules, and the active terminating group, X, can be elaborated into an anionic group such as a sulfate or phosphate.

By controlling solution and substrate chemistry, thin films of “biological” ceramics such as calcium carbonate or calcium phosphate (apatite) can be formed as thin films on the functionalized surface. In the same way, more traditional, “commercial” ceramics such as  $\text{Fe}_2\text{O}_3$  and CdS can be laid down. Combining the lay-down of films such as in [Figure 7.3](#) with state-of-the-art patterning techniques such as photolithography, one can produce films which are intricately patterned.

To summarize, biomimetic coating techniques have the advantages of low temperature and cost, environmentally benign processing, and films which are dense and crystalline and do not require subsequent thermal treatments. Complex shapes and porous materials can be coated in this way. The techniques are compatible with a wide variety of substrates, including temperature-sensitive polymers. Excellent microstructural control is possible, including the production of micrometer-scale patterns. There are, however, significant challenges for these techniques. Solution and substrate conditions must be carefully controlled to ensure successful film production. Also, determining which given ceramic film can be successfully grown on a given surface functional group is largely an empirical process.

Biomimetic ceramic thin films have a broad range of potential industrial applications. An especially attractive possibility in the automotive industry is wear-resistant coatings on polymeric gears. Also, applying hard, optical coatings on polymers could produce an interesting alternative to conventional window

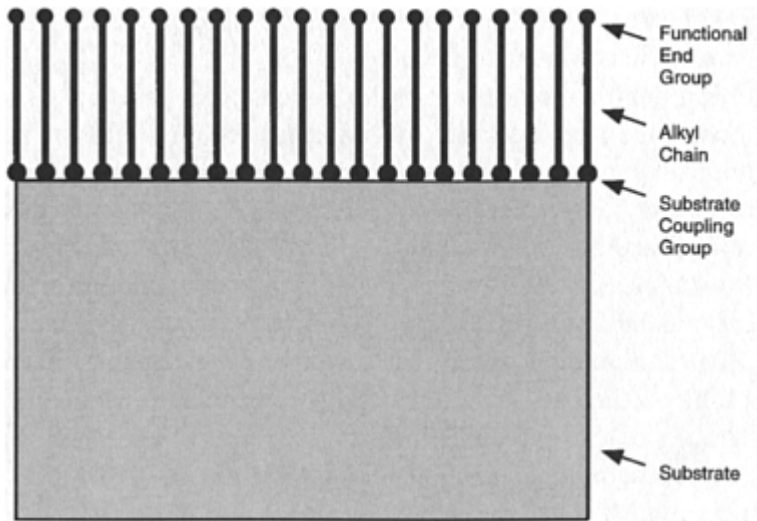


FIGURE 7.3 Schematic illustration of self-assembled monolayer (SAM) on a surface. (After Bunker, et al. 1994)

glass, thus reducing vehicle weight. Patterning capabilities for biomimetics would, of course, have applications in the microelectronic and optoelectronic industries.

As noted at the outset of this chapter, biomimetic processing can come full circle when this technology based on biological principles is used to make materials which can be used in biomedical applications. An interesting example is given in [Figure 7.4](#). In this case, a SAM-treated titanium implant alloy has been coated with a film of insoluble octacalcium phosphate (OCP). The OCP coating is a precursor to apatite formation, thus improving the adhesion between the implant and bone. This coating is competitive with the plasma-sprayed hydroxyapatite coatings discussed in [Section 6.1.1](#). The biomimetic OCP coatings tend to be less soluble and produce less clogging of the alloy's open porosity.

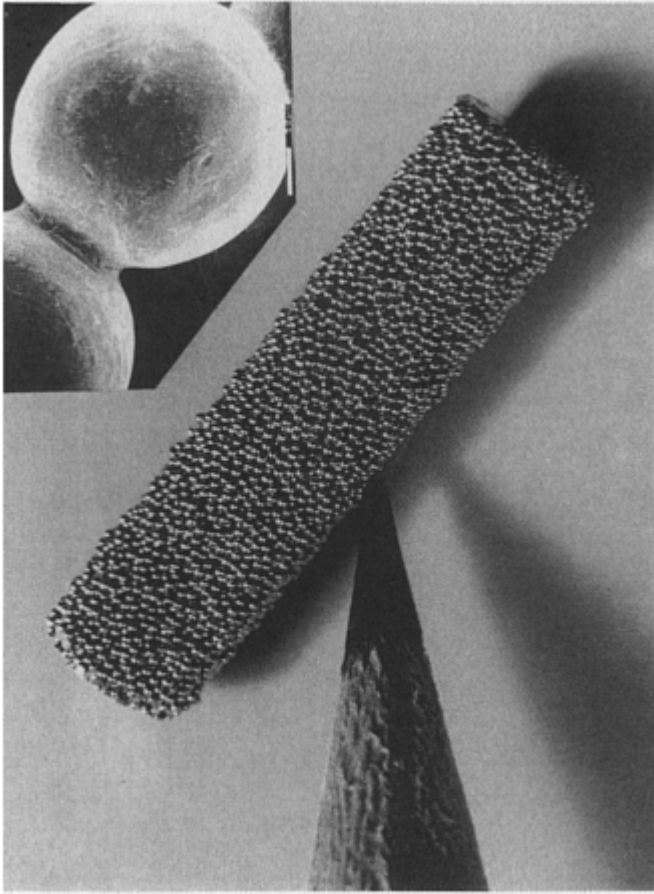


FIGURE 7.4 Biomimetic processing was used to produce a thin coating of octacalcium phosphate (a precursor to hydroxyapatite formation) on this porous titanium implant. (After Bunker, et al. 1994) (See [Color Plate IV](#))



## *Glossary*

Following are definitions of the key words from each chapter. These key words were designated by the use of *italics*.

**abrasive wear** Wear occurring when a rough, hard surface slides on a softer surface. Grooves and wear particles form on the softer surface.

**adhesive wear** Wear occurring when two smooth surfaces slide over each other. Fragments are pulled off one surface and adhere to the other.

**advanced composites** Synthetic fiber-reinforced composites with relatively high modulus fibers. The fiber modulus is generally higher than that of the E-glass used in the traditional composite, fiberglass.

**allograft** Bone defect repair using cadaver bone.

**autograft** Bone defect repair using bone harvested from another part of the body.

**bioceramic** A ceramic material created for an application in biology and medicine.

**biocompatibility** Long term physiologic compatibility.

**Bioglass** Silicate glass designed to bond directly to bone.

**biological material** A naturally occurring structural material, such as bone.

**biomaterial** An engineered material created for an application in biology and medicine.

**biomimetic processing** A ceramic fabrication technique which imitates natural processes, such as sea shell formation.

**bone defect** Centimeter-scale gap in the skeletal system.

**ceramic** Nonmetallic, inorganic engineering material.

**ceramic-matrix composite** Composite material in which the reinforcing phase is dispersed in a ceramic.

**chitin** A cellulose-like biological material and second only to collagen as a component of connective tissues in animals.

**coefficient of friction** Proportionality constant between a friction force attempting to move an object along a surface and the normal force on the object.

**collagen** A natural, polymeric protein which constitutes over one-third of bone by weight.

**composite** Material composed of a microscopic-scale combination of individual materials from the categories of metals, ceramics (and glasses), and polymers.

**concentration cell** Electrochemical cell in which the corrosion and associated electrical current are due to a difference in ionic concentration.

**corrosion** The dissolution of a metal into an aqueous environment.

**corrosion prevention** Use of ceramic and glass coatings to shield metals from environmental degradation.

**corrosive wear** Wear that takes place with sliding in a corrosive environment.

**dental porcelain** A glassy coating on a metal alloy substrate for the repair of diseased or decayed teeth.

**dentin** A biological material found in teeth and more highly mineralized than bone.

**ductility** Deformability, e.g., the percent elongation at failure.

**elastic deformation** Temporary deformation associated with the stretching of atomic bonds.

**electromotive force series** Systematic listing of half-cell reaction voltages.

**engineering strain** Increase in sample length at a given load divided by the original (stress-free) length.

**engineering stress** Load on a sample divided by the original (stress-free) area.

**firing** The processing of a ceramic by heating raw materials to a high temperature, typically above 1000°C.

**flexural strength** Failure stress of a material, as measured in bending.

**fracture mechanics** Analysis of failure of structural materials with preexisting flaws.

**fracture toughness** Critical value of the stress-intensity factor at a crack tip necessary to produce catastrophic failure.

**friction** The resistance to motion when a solid is moved or attempted to be moved.

**galvanic cell** Electrochemical cell in which the corrosion and associated electrical current are due to the contact of two dissimilar metals.

**galvanic series** Systematic listing of relative corrosion behavior of metal alloys in an aqueous environment.

**glass** Noncrystalline solid, unless otherwise noted, with a chemical composition comparable to a crystalline ceramic.

**glass-ceramic** Fine-grained, crystalline ceramic produced by the controlled devitrification (i.e., crystallization) of a glass.

**hydroxyapatite** A calcium phosphate which is the primary mineral content of bone.

**inert** Tendency to exhibit relatively low levels of reactivity which peak on the order of  $10^4$  days (over 250 years).

**materials science and engineering** Label for the general branch of engineering dealing with materials.

**materials selection** Decision that is a critical component of the overall engineering design process.

**metal** Electrically conducting solid with characteristic metallic bonding.

**modulus of elasticity** Slope of the stress-strain curve in the elastic region.

**modulus of rupture** See *Flexural strength*.

**net-shape processing** Material processing which does not require a subsequent shaping operation.

**oxide ceramic** Compound between an elemental metal(s) and oxygen.

**oxygen concentration cell** Electrochemical cell in which the corrosion and associated electrical current are due to a difference in gaseous oxygen concentrations.

**polymer** Engineering material composed of long-chain or network molecules.

**polymethylmethacrylate (PMMA)** Polymer used as a “cement” for fixation of hip prostheses.

**property** Observable characteristic of a material. resorbable Tendency to exhibit high levels of chemical reactivity with the environment, peaking on the order of 10 days.

**silicate** Ceramic or glass with silicon dioxide as a major constituent.

- sol-gel processing** Technique for forming ceramics and glasses of high density at a relatively low temperature by means of an organometallic solution.
- strain hardening** The strengthening of a metal alloy by deformation.
- stress cell** An electrochemical cell in which corrosion can occur due to the presence of variations in the degree of mechanical stress within a metal sample.
- stress-versus-strain curve** General result of a complete tensile test.
- surface fatigue wear** Wear occurring during repeated sliding or rolling of a material over a track.
- surface reactive** Tendency to exhibit a moderate level of chemical reactivity with the surrounding environment, peaking on the order of 100 days.
- tensile strength** The maximum engineering stress experienced by a material during a tensile test.
- tensile test** Mechanical test illustrated by [Figure 3.1](#).
- tricalcium phosphate** A highly reactive bioceramic which tends to be readily resorbed by the body.
- wear** Removal of surface material as a result of mechanical action.
- yield strength** The strength of a material associated with the approximate upper limit of its linear, elastic behavior.

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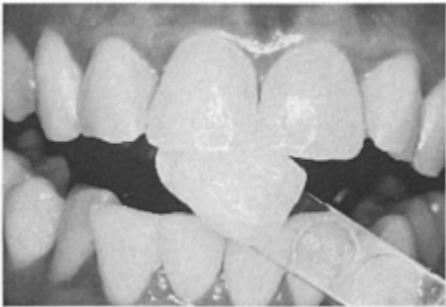
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Color Plate I. See [Figure 6.2](#), Page 50.

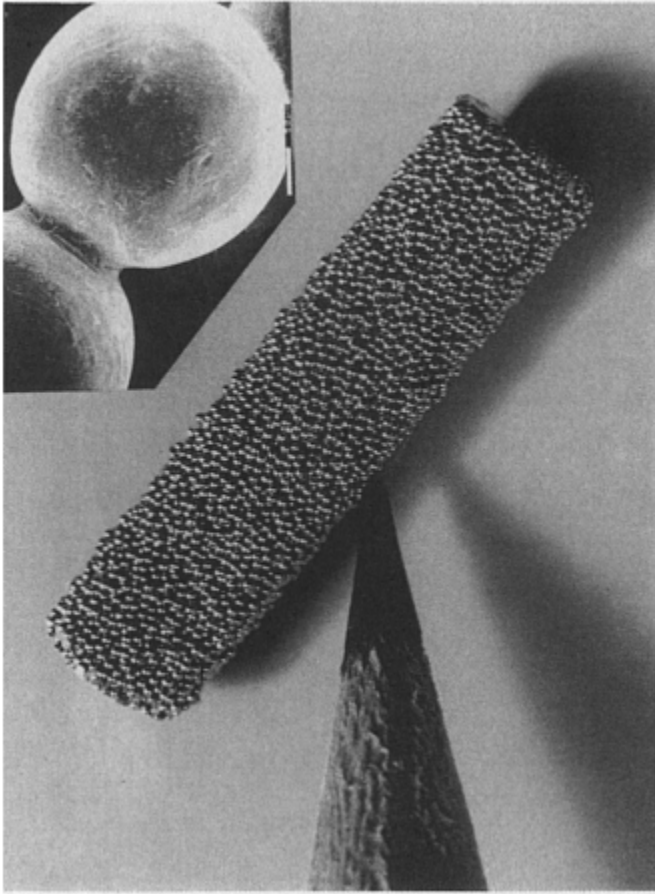


Color Plate II. See [Figure 6.3](#), Page 55.



Color Plate III. See [Figure 6.4](#), Page 58.





Color Plate IV. See [Figure 7.4](#), Page 69.

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